Hydrogenation of Nitrile and Olefinic Groups in Butadiene Rubbers

by

Minghui Liu

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Nowadays, traditional diene-based polymers cannot meet the demand for robust elastomers in many industries. Acrylonitrile butadiene rubber (NBR) is a widely used diene-based polymer as an oil-resistant elastomer and is produced via copolymerization of acrylonitrile (AN or ACN) and butadiene (BD). When dealing with aggressive environments, NBR's performance decreases rapidly due to the residual carbon-carbon double bonds in the polymer backbone. By selectively hydrogenating these unsaturated bonds to yield its more stable counterpart, hydrogenated NBR (HNBR), the mechanical, thermo-oxidative and chemical resistant properties of a material are greatly improved. The ACN content of NBR and HNBR also determines a number of properties including oil and solvent resistance, compatibility with polar solvent and abrasion resistance etc. HNBR with lower ACN content can be cured without sulfur which improves heat resistance and is much more environmentally friendly.

In the present research project, a rhodium hydrido complex was screened and synthesized; a corresponding catalytic system was successfully established to produce HNBR with a certain amount of ACN. It is worthwhile to point out that this thesis is the first development in establishing a system that is able to reduce nitrile content of the macromolecular polymers (NBR and HNBR), and to achieve tandem hydrogenation of both nitrile groups and olefinic groups in the macromolecular polymer (NBR).

In both HNBR and NBR systems, the nitrile content can be reduced from 40% to less than 10% within 5 hours at 60^{o}C and 500 psig H_2. The nitrile groups have been converted to primary amines without any side products such as the formation of secondary amines. A possible mechanism for nitrile reduction has been proposed for the first time. The causes for gel formation during nitrile reduction have been investigated and a possible mechanism is proposed. Several additives have been tested and some of them are found to be effective to slow down or terminate gel formation, and tryphenylphosphine (TPP) was found to be the most effective additive. In the NBR system, tandem hydrogenation of nitrile and olefinic groups has been successfully achieved. The nitrile reduction process is similar to that of the HNBR system. The olefinic groups were reduced from 100% to lower than 5% simultaneously under the same reaction conditions. A possible mechanism for tandem hydrogenation has also been proposed for the first time.

An effective catalytic system for the hydrogenation of carbon-carbon double bonds in styrene butadiene rubber (SBR) was successfully developed using the same Rh catalyst. In the absence of any additives, the C=C bonds in SBR were hydrogenated to more than 95% in a relatively short period of time and no cross-linking was observed. Optimization of experimental conditions has been carried out for eco-friendly and energy-saving purposes. Different experimental parameters have been studied. The properties of SBR did not change after hydrogenation of the unsaturated C=C bonds. This study provides a new route for the chemical modification of SBR by using a transition metal complex.

Additionally, NBR in the form of latex has been successfully hydrogenated to high conversion by using $RhCl_3$ without any organic solvent. NBR latex can be hydrogenated to a degree of more than 95% within 5 hours at 160^oC using $RhCl_3$ in the presence of triphenylphosphine (TPP). Various experimental parameters were investigated. Wilkinson's catalyst is synthesized *in situ* during the hydrogenation. TPP is the co-catalyst ligand in the latex hydrogenation using $RhCl_3$ and also a catalyst mass transfer promoter and reducing agent. Ethanol is a very effective co-solvent for TPP and $RhCl_3$ (but not for the rubber).

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At last, to my beloved parents for their support and love!

Dedication

In Memory of Dr. Jialong Wu (1971 - 2010)

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Chapter 1
Introduction

1.1 Overview of Polymer Hydrogenation

Monomers containing at least two carbon-carbon double bonds (C=Cs) can be used to form diene-based polymers. These monomers include butadiene, isoprene and chloroprene. Diene-based polymers, such as polybutadiene and polyisoprene, usually contain these diene moieties and/or other olefinic monomers where at least one monomer is a diene, e.g. acrylonitrile-butadiene copolymer (NBR). Olefinic structures are common in diene-based polymers. Those polymers are very useful to scientists and engineers due to their desirable physical properties and that they can be used as a base polymer for some important chemical modification processes.

An important area of research in polymer chemistry is the chemical modification of diene-based polymers,[1,2] as it can lead to the development of polymers with chemical and physical properties that cannot be achieved by normal polymerization methods.[3] The range of application of unsaturated polymers has been extended as methods to modify these polymers via the hydrogenation of C=Cs have been examined. These polymers have been hydrogenated with the aid of metal catalysts, for example, hydrogenated acrylonitrile butadiene rubber (HNBR) has been obtained by the use of noble metal catalysts (including ruthenium and rhodium complexes) which can be very expensive.[4] Furthermore, these catalysts can be lost during the synthesis process as they are difficult to separate from the polymer product. Recently, catalysts that do not contain noble metals have been studied for the hydrogenation of acrylonitrile butadiene rubber (NBR), including hydrazine hydrate/sodium periodate[4] and selenium catalysts[5,6].

One of the desirable properties attributed to hydrogenated polymers is their excellent thermal and oxidative stability. As an example, Kraton G® (Royal Dutch Shell plc), a hydrogenated styrene-butadiene-styrene copolymer, displays exceptional weather ability and thermal, oxidative and UV stability and has been used in laminating films, high performance adhesives and sealants. Another hydrogenated polymer, hydrogenated acrylonitrile-butadiene rubber (HNBR), Therban® (Lanxess Inc.), has exhibited excellent thermal stability and resistance to oil and chemicals, and has been used in seals, hoses and belts for cars and in oilfields. Improved thermal and oxidative stability has also

been shown for hydrogenated polystyrene (HPS) and polycyclohexylethylene[7,8] along with improved optical properties.

1.2 Significance of Hydrogenating Olefinic and Nitrile Groups in NBR

Acrylonitrile butadiene rubber (NBR) is a widely used diene-based polymer prevalent in industry as an oil-resistant elastomer and is produced via emulsion copolymerization of acrylonitrile and butadiene. Due to recent developments in the automotive and oil industries, the polymer is required to retain high thermal stability and long-time oil resistance in aggressive surroundings. Hydrogenated NBR emerged as the most promising elastomer, although fluoro-elastomers (FKM) and fluro-silicone (FMQ) were also considered, as they demonstrate excellent mechanical properties, good oil resistance, and high-temperature performance and are accessible at a reasonable price as well. A typical industrial catalytic process of HNBR production is shown in Figure 1-1.

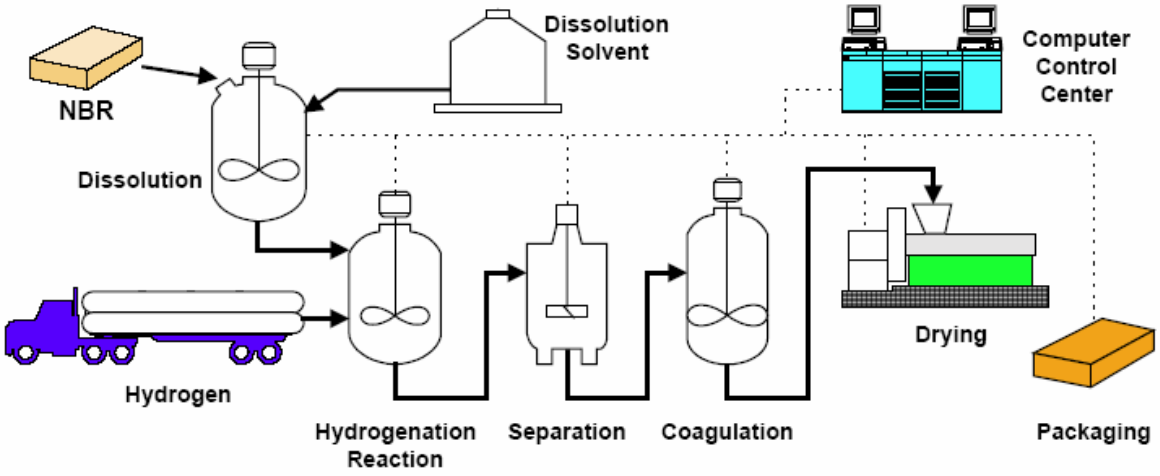


Figure 1-1 HNBR production process[9]

The acrylonitrile (ACN) content is used to define the grade of NBR. Due to polarity, the ACN content can determine a number of properties including oil and solvent resistance and abrasion resistance. Higher ACN content improves fuel and polar lubricant resistance of HNBR while worsening its low-temperature properties.[10] Properties such as air/gas impermeability, abrasion resistance, tensile strength and compatibility with other polar polymers will improve with higher ACN content [11]. Lower ACN content has the opposite effect and decreases fuel and polar lubricant resistance while improving HNBR's low-temperature properties.[10] Properties such as compression set, flexibility,

resilience and hysteresis will all improve with lower ACN content.[11] The ACN content can be varied from 17-49% with the standard being in between 35-45%.[10]

Typically, HNBR can be either sulfur-cured or peroxide-cured. Sulfur curing improves flexibility in dynamic systems but reduces heat resistance and creates an inferior compression set.[10] NBR with higher ACN content will cure at a faster rate with sulfur curing systems while NBR with lower ACN content will cure at a faster rate with peroxide curing systems.[11]

1.3 Scope of This Research

Over the past decades, the technology for manufacturing HNBR has been widely investigated and successfully commercialized by Lanxess Inc. and Zeon Corporation. In the meantime, hydrogenation of small-molecular nitriles to amines, aldehydes and hydrocarbons have also been a very popular topic. However, hydrogenation of nitriles (or nitrile groups) in macromolecules or polymers has hitherto never been studied or achieved; not to mention that no one has ever been able to hydrogenate olefinic and nitrile groups in a polymer at the same time.

The aim of this research is to explore the feasibility of reducing nitrile groups in diene-based polymers, and to discover and establish an effective catalytic system for tandem hydrogenation of both olefinic and nitrile groups in macromolecular polymers like acrylonitrile butadiene rubber (NBR). A certain amount of ACN content in HNBR will not only improve fuel and polar lubricant resistance and properties such as air/gas impermeability, abrasion resistance, tensile strength and compatibility with other polar polymers, but also improve HNBR’s low-temperature properties (compression set, flexibility, resilience and hysteresis). In addition, HNBR with lower ACN content can be cured without sulfur which improves heat resistance and will be much more environmental friendly.

As is well known, Prof. Garry Rempel's research group has been working in the field of modification of the olefinic group in polymers for several decades and has made prolific achievements in the hydrogenation of a variety of diene-based rubbers in different forms such as solution, bulk and latex. In the search for alternate and novel catalysts for NBR latex hydrogenation, it was found that some transition metal catalysts were capable of reducing the acrylonitrile content of butadiene rubber, a feature which had drawn our attention.

With the previous research experience of our group and the study of academic and industrial progress in nitrile reduction in the past, a wide range of rhodium and ruthenium catalysts have been chosen as

the experimental subjects. Through great efforts over almost a year, a rhodium hydrido complex (the catalyst) was screened out, successfully synthesized with a series of modifications in synthetic procedures and shown in this study to be effective for nitrile hydrogenation in butadiene rubbers for the first time. Moreover, this thesis is the first time to achieve tandem hydrogenation of olefinic and nitrile groups in NBR.

To make the start relatively easier, hydrogenated acrylonitrile butadiene rubber (HNBR) was first chosen as a model, because more than 95% of the carbon-carbon double bonds have already been removed and there is only nitrile groups left as the target. Afterwards, the screened catalysts have been used with acrylonitrile butadiene rubber (NBR) to hydrogenate both olefinic and nitrile groups. As an effective and versatile catalyst, it also shows very promising performance in hydrogenation of styrene butadiene rubber (SBR). In all of the above cases, optimal experimental conditions have been established, including catalyst/rubber ratio, H_2 pressure, reaction temperature, agitation speed etc. Preliminary study of the rheological properties of the final products has also been carried out.

One of the biggest problems and most difficult challenges in the rubber industry is how to prevent or minimize gel formation during the hydrogenation process. This problem as encountered in this study as well. A lot of valuable and successful work has been conducted to reduce, minimize and control the cross-linking and gel formation in both NBR and HNBR systems.

At last, after developing a new hydrogenation route which has the potential of being commercialized, a series of recommended future work have been outlined, such as scale-up of the reaction system, search for alternate catalysts in terms of lower cost and easier recovery, feasibility of tandem polymerization and hydrogenation, or tandem hydrogenation and vulcanization, in butadiene rubbers, and more profound and systematic study of reaction kinetics and catalyst recovery etc.

Chapter 2
Literature Review

2.1 Hydrogenation of Diene-based Polymers

Nowadays, traditional diene-based polymers cannot meet the demand for robust elastomers in many industries.[12,13] For instance, in the automobile industry engine compartment temperatures have been greatly increased as a result of more efficient power trains, requiring key rubber components, such as hoses, seals and timing belts, with improved mechanical, thermal and chemical properties.[14,15] McGrath *et al*. found that the modification of diene-based rubbers is an efficient synthetic route and most of the modifications have focused on improving thermal and oxidative stability.[16]

2.1.1 Hydrogenation of NBR

Among diene-based rubbers, nitrile butadiene rubber (NBR) is widely used in oil and gas production equipment and engine delivery systems,[17] due to its extraordinary oil and solvent resistance. NBR is synthesized through emulsion copolymerization of butadiene (Bd) and acrylonitrile (AN or ACN). After the polymerization, there is still a residual carbon-carbon double bond left in each Bd segment in the final polymer as shown in Figure 2-1. When dealing with sour gas, oxidized fuel and aggressive solvents especially at high temperature, the rubber's performance decreases rapidly, because the residual carbon-carbon double bonds in the polymer backbone are prone to degradation when exposed to light, heat or ozone. By selectively hydrogenating these unsaturated bonds, the reactivity of the material in resistance to aggressive environments has been sharply reduced, thereby extending its range of application. A leading sample is the catalytic hydrogenation of NBR to yield its more stable counterpart, hydrogenated NBR (HNBR). Several catalysts have been developed to selectively hydrogenate the carbon-carbon double bonds and leave the nitrile groups intact.[18]

Hydrogenated nitrile butadiene rubber (HNBR) has excellent mechanical, thermo-oxidative and chemical resistant properties over a wide operating temperature range, particularly after being exposed for a long-term exposure to heat, oil, and chemicals. Its unique properties have resulted in wide utilization of HNBR in the automotive, industrial, and various performance-demanding areas. Based on volume, the automotive market is the largest, using HNBR for a host of dynamic and static seals, hoses, and timing belts. HNBR has also been widely adopted in industrial sealing for oil field exploration and processing, as well as rolls for steel and paper mills.

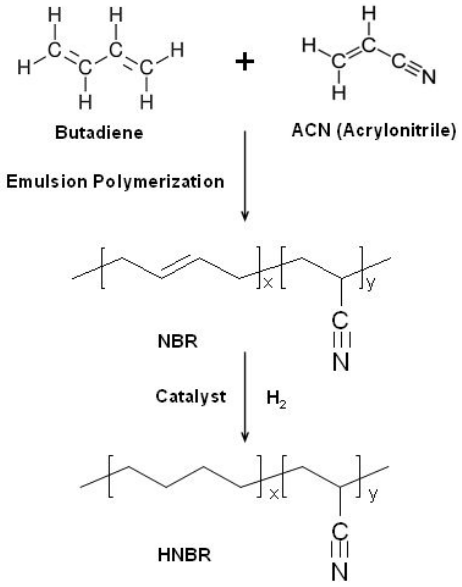


Figure 2-1 Hydrogenation of NBR

2.1.2 Hydrogenation Kinetics

The reaction kinetics and mechanism of the catalytic hydrogenation of NBR has been thoroughly investigated over a wide range of experimental conditions for a rhodium catalyst[19,20] and for an osmium catalyst.[18] It was shown that the olefin conversion obeys a first order rate model with respect to carbon-carbon double bond concentration and catalyst concentration. However, it could vary from zero order to second order with regard to hydrogen concentration, depending on different operating conditions such as pressure of the catalytic system. In principle, the kinetics for hydrogenation carried out at a given catalyst concentration can be described as,

$$-\frac{d[C=C]}{dt} = k'\cdot[C=C]\cdot[H_2]^m$$

wherein, the reaction order *m* varies from 0 to 2.

For homogeneous catalyst precursors, $RhCl(PPh_3)_3$ and $RhH(PPh_3)_3$, the NBR hydrogenation exhibits a first-order olefin dependence. For both catalytic systems a first- to zero- order dependence on hydrogen is observed as the system pressure is increased. However, for the $OsHCl(CO)(L)(PCy_3)_2$ ($L=O_2$) catalyst complex the reaction order decreases from a second order to a zero order dependence when the hydrogen pressure exceeds 60 bars.[21] Strict first order behavior in hydrogen is maintained for the ruthenium analogue $RuHCl(CO)(PCy_3)_2$.

2.1.3 Cross-linking in Polymer Hydrogenation

The crosslinking mechanism during the hydrogenation of diene-based polymers is not well understood to date. When using Ru catalysts for hydrogenating NBR, it has been observed that an increase in molecular weight results in the formation of gel. It has been hypothesized that the gelling problem occurs via a Michael-type addition.[22] Certain additives, however, have been shown to have a beneficial effect on minimizing gel formation. Organic additives such as chloroacetic acid, hydroxyl acetic acid, ascorbic acid and phenoxy acetic acid were added to an NBR emulsion that was hydrogenated in methyl ethyl ketone (MEK) at 2.5 to 10.0 MPa hydrogen pressure and 100 to 200ºC. The additives decreased the gel content. Phenylhydrazine has been shown to be effective in breaking cross-links[23] and hydroquinone has been shown to significantly reduce the mass fraction of gel in hydrogenated NBR.[24,25] It was also shown that inhibitors, such as 2-6-di-tert-butyl-4-methyl phenol (DTBMP), reduced the gel content by over half while subsequently increasing the degree of hydrogenation (when compared to hydroquinone).[25]

2.2 Hydrogenation of Nitriles

Nitrile hydrogenation is a common industrial practice in production of amines. Amines have a wide variety of applications “as solvents, intermediates for pharmaceuticals, raw materials for resins, textile additives, disinfectants, rubber stabilisers, corrosion inhibitors and in the manufacture of detergents and plastics”.[26] While several methods exist to produce these amines, catalytic hydrogenation of nitriles is most common.

Hydrogenation of nitriles will always produce secondary and tertiary amines along with the desired primary amine. “As known, conversion of the nitrile group to a primary amine takes place relatively easily, but the selectivity of the reaction can strongly decrease due to secondary or tertiary amines forming in side-reactions”.[27] Selectivity for each type of amine can be changed through changes in the catalyst used, temperature and pressure changes as well as addition of ammonia to the reaction. It is believed that excess secondary and tertiary amines lead to gelling of the rubber and thus selectivity toward primary amine production is important.

2.2.1 Reaction Mechanism

Catalytic hydrogenation of nitriles has been widely studied for small molecular nitriles. That being said that hydrogenation of nitriles in polymers has yet to be reported or published. Braun *et al.*[28] proposed basic mechanisms for the hydrogenation of nitriles in 1923 as shown below.

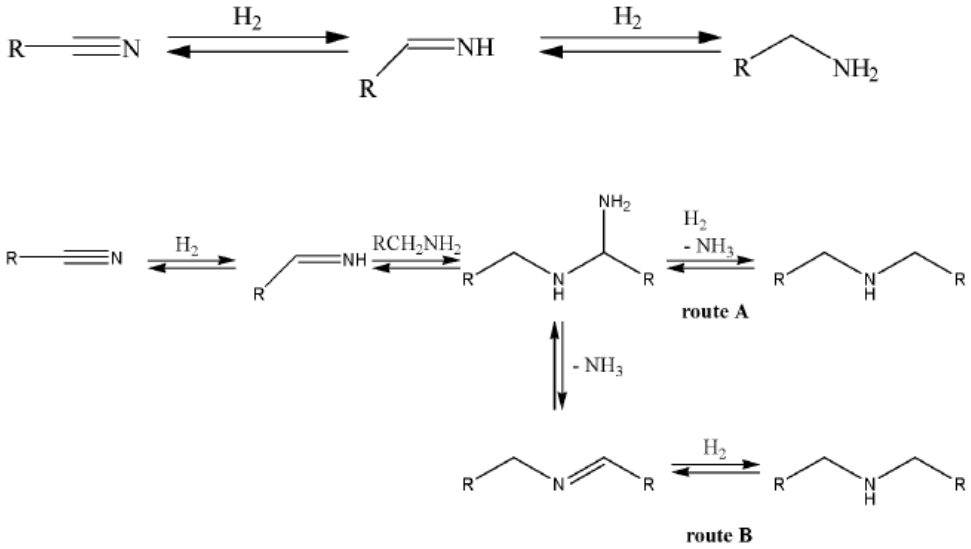


Figure 2-2 Mechanism for hydrogenation of nitriles as proposed by Braun *et al.*[28]

These mechanisms have been widely accepted since their proposal. The diagram below, produced by Volf and Pasek,[29] expanded on Braun's mechanism and provided a summary of typical hydrogenation reactions A, B, E and H. The other reactions, C, D, F and G, describe an acid-base catalyzed condensation. The diagram also displays the different reactions in which primary, secondary and tertiary amines can be formed:

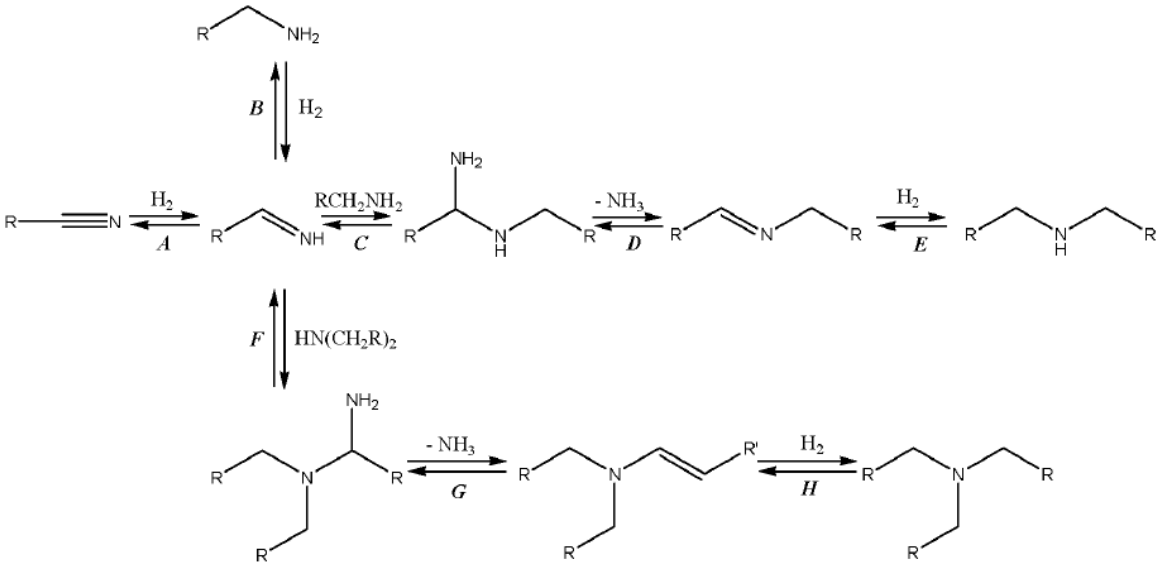


Figure 2-3 Hydrogenation of nitriles including acid-base catalyzed condensation and formation of secondary and tertiary amines[29]

Verhaak *et al.* [30] proposed a different mechanism, as shown in Figure 2-4, for the hydrogenation of acetonitrile in the gas phase using a nickel catalyst. The reaction was reduced in acidity and a potassium promoter was added to gain higher selectivity to the primary amine.

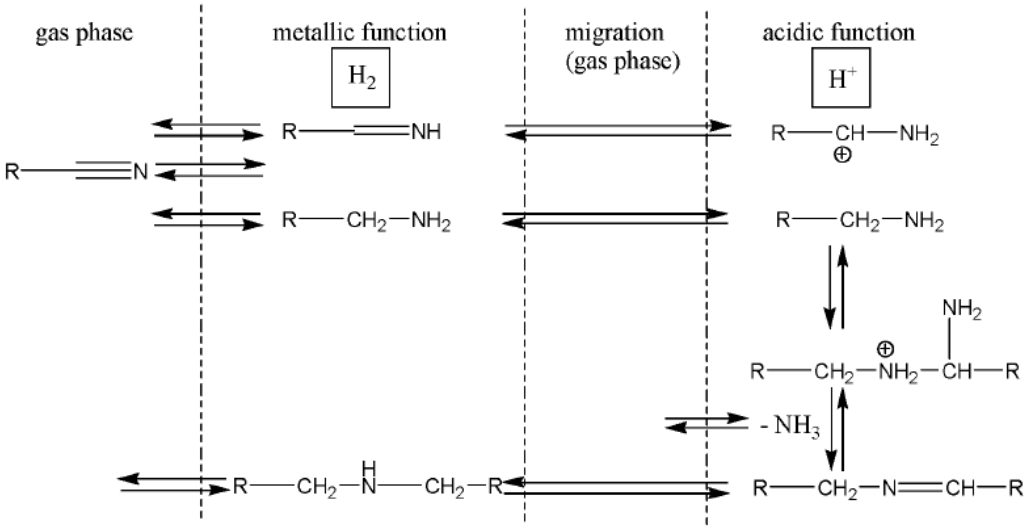


Figure 2-4 Hydrogenation of acetonitrile in gas phase under nickel catalyst depicting formation of various amines as proposed by Verhaak *et al.*[30]

Side products are also formed during hydrogenation. Nucleophiles like water can attack the cyano carbon or even an imine carbon.[31] Dimerisation is another common side product in hydrogenation of nitriles.[32] Catalysts themselves can also cause side reactions to occur depending on their composition and the ligands attached. These unwanted reactions often result in C-N, C-C and/or C-O formation. Formation of these by-products reduces the amount of primary amine present in solution. In hydrogenation of nitirile groups in HNBR and NBR, this may lead to gelling of the final product. De Bellefon and Fouilloux[31] describe some of the many side reactions that can form by-products during hydrogenation:

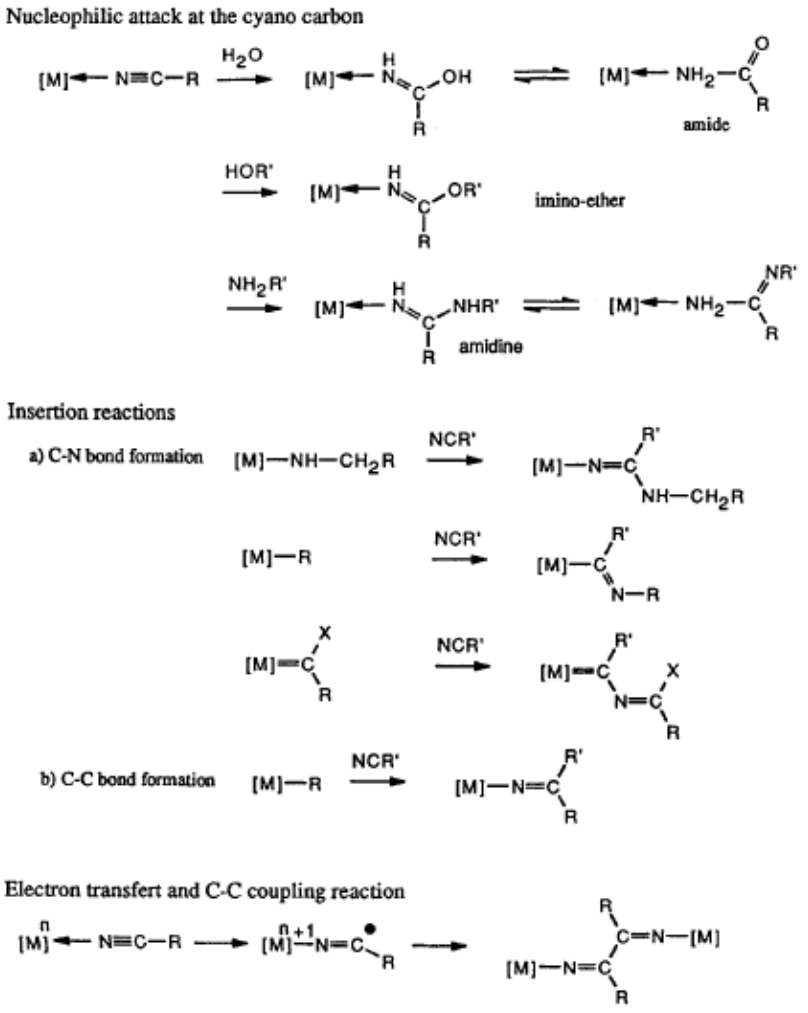


Figure 2-5 Various side-reactions that occur during hydrogenation of nitriles[31]

2.2.2 Heterogeneous Hydrogenation of Nitriles

Heterogeneous catalysts are named such as they are of a different phase from the substance that they are catalyzing. Heterogeneous catalysts tend to be less selective toward a primary amine, producing more secondary and tertiary amines. That being said, addition of NH_3 or acidic additives can enhance selectivity for the primary amine. NH_3 can suppress the dissociation of NH_3 from amines and from the generation of secondary and tertiary amines as well as those formed from imines. Acids react with primary amines to form salts which can then protect the primary amine (refer to Figure 2-6).

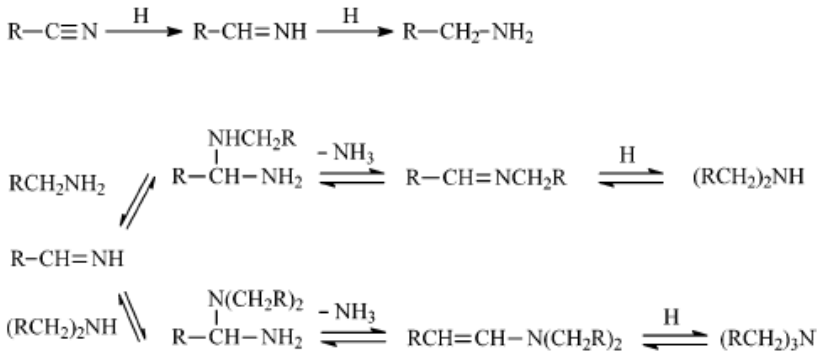


Figure 2-6 Formation of imine, primary, secondary and tertiary amines in nitrile hydrogenation

Pd, Ni, Co and Fe etc. have been used for the heterogeneous hydrogenation of nitriles, although Ni and Pd are most commonly used. These metals have variable oxidation states that make many different catalyst/ligand combinations possible. On occasion heterogeneous catalysts can even be recovered. Heterogeneous hydrogenation also allows for interaction with surface chemistry and surface catalysis. This surface chemistry is important in determining a catalyst's activity and selectivity. Hegedus *et al*.[27] looked at acid sites on a particular catalyst which they examined stating that, “Neutralization of acid sites was therefore postulated to interpret the better selectivity to primary amine in the hydrogenation of primary nitriles over Raney-type Ni catalysts in the presence of NaOH.” By modifying the surface chemistry via neutralization of acid sites on the catalyst they were able to obtain better selectivity for the primary amine.

Table 2-1 lists a few heterogeneous processes for nitrile hydrogenation. For #1, #2 and #4 palladium catalysts were used. The reaction systems in #1 and #2 are actually biphasic system, including organic phase and water phase. The generated primary amines react with NaH_2PO_4 and the formed salts are then transferred from organic phase to water phase, so that the primary amines are protected. After the addition of NaH_2PO_4, the selectivity was about 95% for the hydrogenation of benzonitrile and

40% for the hydrogenation of benzyl cyanide. The reason for the poor selectivity in #2 could be that the absorption of the imine species on the catalyst is not as good as that in #1.

Table 2-1 Heterogeneous hydrogenation of nitriles[26,27,33]

#	Catalyst	Reaction conditions and results
1	Pd over C, Al_2O_3, TiO_2	Benzonitrile, water/organic, NaH_2PO_4 (2:1 mol), ~100% conversion, ~95% selectivity, 30°C, 6 bar
2	Pd/C	Benzyl cyanide, water/organic, NaH_2PO_4 (2:1 mol), ~100% conversion, ~40% selectivity, 40°C, 6 bar
3	Raney Ni	Benzonitrile (0.78 mol/L), 2-propanol, liquor ammonia (6% vol in mixture), ~99% yield, 80°C, 15 bar, Ni 5%
4	Pd/MCM-41	Benzonitrile, SC-CO_2 (10 MPa), H_2 2 MPa, 50°C, 90% conversion, 91% selectivity

In #3 Raney nickel was used as a catalyst and an alcohol as solvent. After the addition of ammonia, the yield of benzylamine was increased from 35% to 99%. In #4, supercritical CO_2 (SC-CO_2) was used as solvent. It was found that the selectivity changed along with the pressure of CO_2. Under suitable conditions the selectivity was increased to 91%. Xie *et al.*[33] investigated the hydrogenation of nitriles in CO_2-expanded solvent in both heterogeneous (Ni) and homogeneous (Rh) systems, and reported that the selectivity was improved for the heterogeneous system and yield was improved for the homogeneous system in the presence of CO_2. It was deemed that the amines were protected by CO_2 as follows:

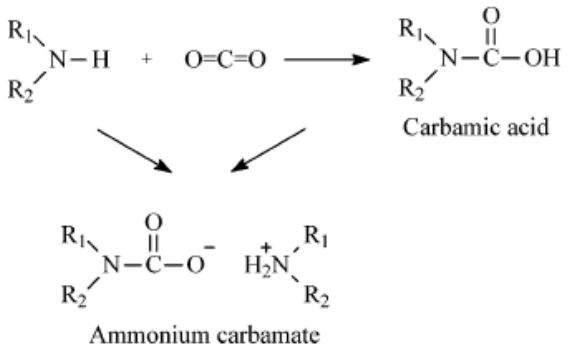


Figure 2-7 Role of CO_2 in the protection of amine

In the heterogeneous system with the introduction of additives, the selectivity has been markedly improved. However there are still two main disadvantages with the catalytic system. 1) Side products such as secondary and tertiary amines cannot be totally eliminated. In the case of hydrogenation of polymer-based nitriles like NBR, trace formation of secondary and tertiary amines may lead to the gel formation of the polymer. 2) The contamination of additives gives rise to the separation and recovery issues. It has been shown that selectivity has been markedly improved through the introduction of additives to a heterogeneous system. NH_3 is commonly used to increase selectivity for primary amines during hydrogenation of nitriles. Although additives like NH_3 can increase selectivity, they can also react with the ligand of the catalyst or other chemicals in the treated solution. This contamination causes separation and recovery issues with the catalyst.

2.2.3 Homogeneous Hydrogenation of Nitriles

Homogeneous catalysts are those in the same phase with the substance being catalyzed. Rhodium, ruthenium, nickel and iridium based catalysts are by far the most commonly used homogeneous catalysts. These metals are able to adopt several oxidations states allowing many different-ligand complexes to be formed and tailored toward a specific reaction. Homogeneous catalysts exhibit high selectivity for the primary amine, but are not easily recoverable. These catalysts for the homogeneous hydrogenation of nitriles and imines have been studied. Details are as follows.

2.2.3.1 Rhodium compounds

De Bellefon *et al*.[31] stated that, “phosphine complexes of ruthenium and rhodium are able to perform the hydrogenation at low hydrogen pressure and temperature below 100°C with very good selectivity to primary amine.” While not as active as many heterogeneous catalysts, homogeneous rhodium catalysts are far more selective toward the primary amines under much milder conditions. Hegedus *et al*.[27] also stated “high primary amine selectivities were achieved only with Raney nickel or rhodium catalysts” further supporting this notion.

Rhodium can form up to seven different oxidation states. This versatility allows many different electronic structures around the rhodium center that can be fine-tuned using different ligands. Rao *et al*.[34] stated that “in a descriptive way, in the cyano group, the C≡N bond is relatively very short and strong. This implies that the bonding π orbitals are very low lying in energy and by symmetry the antibonding π* orbitals are of high energy”. Different catalytic structures will react with this cyano group very differently. For hydrogenation of nitriles rhodium(III) dihydrides are believed to be the

most effective catalysts. These catalysts can be synthesized as a rhodium(III) dihydride complex or they can be made through reaction of H_2 with a rhodium(I) complex.

T. Yoshida *et al*.[35,36] reported the hydrogenation of small molecular nitriles using homogeneous rhodium hydrides $RhH(PPr^i_3)_3$ and $Rh_2H_2(\text{-}N_2)\{P(\text{cyclohexyl})_3\}_4$. The second compound is the precursor of a three-co-ordinate rhodium(I) hydride $RhH\{P(\text{cyclohexyl})_3\}_2$. The beauty of these catalysts is that they do not cause the formation of secondary or tertiary amines, which is crucial in the hydrogenation of polymer-based nitriles to suppress gel formation. These catalysts are active for the hydrogenation under ambient conditions. It was also mentioned that they are active for the dehydrogenation of amines to give imines and nitriles at high temperature.

It is thought that the preference of nitriles for binding to a metal center is via the nitrogen lone pair of electrons rather than due to the C≡N triple bond system, thus multi-center catalyst systems should be more efficient. Heterogeneous catalysts usually have multi-centers, which could be the reason why they are more active for the hydrogenation of nitriles though the selectivity is usually low. M. D. Fryzuk *et al*.[37] investigated the reaction between dinuclear rhodium hydrides with nitriles, and proposed a reaction path shown as in Figure 2-8. An intermediate (Figure 2-9) was possibly formed in the reaction.

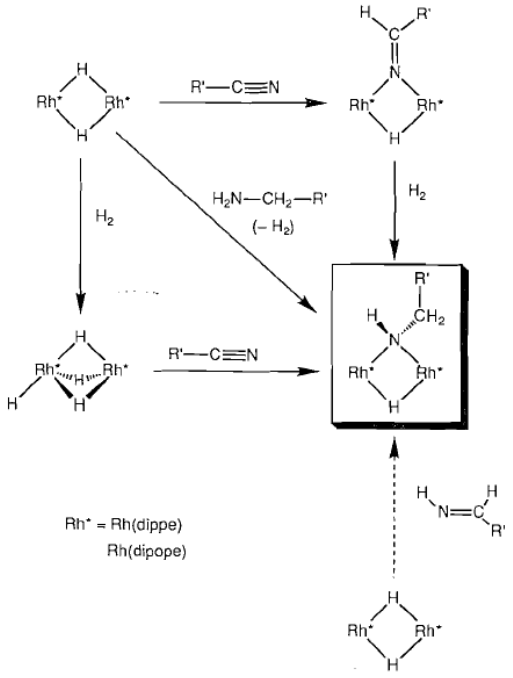


Figure 2-8 Reactions of dinuclear rhodium hydrides with nitriles[37]

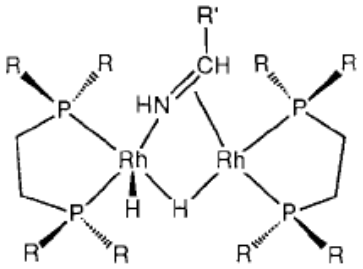


Figure 2-9 Intermediate possibly formed in the hydrogenation of nitriles[37]

The main disadvantage in using rhodium complexes for catalytic hydrogenation of nitriles is its high sensitivity to air. Almost all catalysts must be made under a N_2 or argon atmosphere and must be sealed from air during storage. This can cause complications during synthesis and can limit the ways in which these catalysts react. De Bellefon *et al.*[31] also stated that the problems of catalyst recovery and product separation are strong limitations in the industrial use of these catalysts.

2.2.3.2 Ruthenium Compounds

Similar to rhodium compounds, ruthenium compounds can take on multiple oxidation states and exhibit a high selectivity toward formation of primary amines.[38] Though they tend to have less selectivity than rhodium complexes, ruthenium complexes form more multi-center catalysts. Both complexes remain air sensitive.

M. Joshi *et al.*[39,40] reported the hydrogenation of nitriles with a homogeneous multi-center ruthenium complex $[Ru(H)Cl(dppb)]_3$. When the catalyst was used for the hydrogenation of benzonitrile in a dimethylacetamide (DMA) solution, the highest selectivity reported for the primary amine was 95.5%.

$RuCl_2(PPh_3)_3$[41] has been used for the hydrogenation of benzonitrile in ethanol. When 85% of the theoretical amount of hydrogen was consumed, the yield of benzylamine was 29%, which implies the selectivity was lower than 40%. $RuCl_2(PPh_3)_3$ was further investigated by S. Enthaler *et al.*[42] It was found that with the addition of t-BuOK, the selectivity was increased to higher than 99%, as shown in Figure 2-10. The same research group also developed an *in situ* catalytic system which is composed of Ru(COD)(methylallyl$_2$) with 1,1'-bis(diphenylphosphino)ferrocene(dppf) ligand[43] or NHC ligands[44] for the hydrogenation of nitriles that has higher than 99% of selectivity obtained with the addition of t-BuOK.

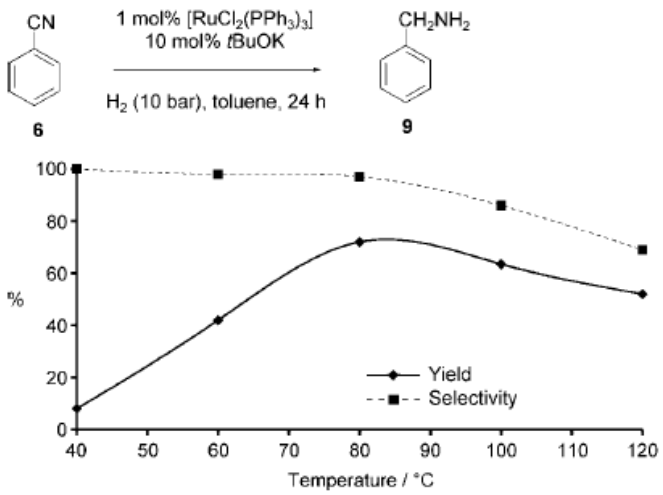


Figure 2-10 Effect of temperature on the reduction of benzonitrile by Enthaler *et al*.[42]

Reaction time = 24 h, $[RuCl_2(PPh_3)_3]$ = 0.0038 mmol, tBuOK = 0.038 mmol, benzonitrile = 0.38 mmol, toluene = 2.0 mL, hydrogen = 10 bar

A. Toti *et al*.[45] investigated the hydrogenation of nitriles catalyzed by $RuH_2(CO)_2(P^nBu_3)_2$, $RuH_2(CO)_2(PPh_3)_2$ and $RuH_2(PPh_3)_4$ without any additives. However under the range of their reaction conditions, both conversion (< 80%) and selectivity (< 50%) were quite low. Ionic ruthenium hydride catalysts $K^+[(Ph_3P)_2Ph_2PC_6H_4RuH_2]^-C_{10}H_8(C_2H_5)_2O$ and $K^+_2[(Ph_3P)_3(Ph_2P)Ru_2H_4]^{2-}{}_2C_6H_{14}O_3$ were used for the hydrogenation of nitriles.[46,47] The highest selectivity for the hydrogenation of acetonitrile was only 65%. H.G. Martin *et al*.[48] prepared ruthenium nanoparticles in nitrile-functionalized ionic liquids for the hydrogenation of benzonitrile. However the main product was a secondary imine. Among the homogeneous hydrogenation of nitriles, most reports are for ruthenium catalysts. With the addition of base, the selectivity is encouraging (> 99%).

2.2.3.3 Nickel Compounds

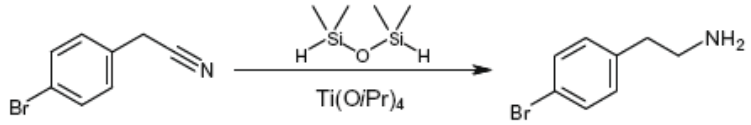
Nickel compounds are among the most popular for hydrogenation of olefins. They are economical, easy-to-make compounds that work very well for standard hydrogenations. However, nickel catalysts fall short in the hydrogenation of nitriles. They are not very efficient or very selective.

Zerecero-silva *et al*.[49] applied a Ni(0) compound for the hydrogenation of mononitriles and dinitriles. Reaction of the catalyst precursor $[(dippe)Ni(-H)]_2$ and benzonitrile forms an active Ni(0)

species [(dippe)Ni(-NC-Ph)]. Tetrahydrofuran (THF) was used as solvent and the reaction temperature was higher than 140°C, with a hydrogen pressure of 60-120 psig. However for benzonitrile, only benzylimine and a trace of dibenzylamine were obtained, with no benzylamine in the product. For dicyanobenzene, a trace of the primary amine, cyanobenzylamine, was obtained. The lack of primary amine could be due to the low pressure of hydrogen. Ni clusters such as $Ni_4(CNR)_7$ has also been tried for the hydrogenation of nitriles.[50] Again the selectivity to primary amine was not high.

2.2.3.4 Alternative Hydrogen Source

Hydrogenation can also be achieved by using strong hydride donors such as aluminum hydrides, boranes or hydrosiloxane derivatives. "The cyano group is ordinarily reduced using either catalytic hydrogenation or a strong hydride donor, such as lithium aluminium hydride, which leaves little scope for selectivity".[32,51,52] Laval *et al*.[53] employed a tetramethyldisiloxane/titanium(IV) isopropoxide reducing system for the hydrogenation of nitriles. Some results are shown in Figure 2-11. One can see the highest selectivity is about 96%. Separation of byproducts TiO_2 and oligomeric siloxanes is also a concern.



1a — toluene, 60°C, 24h — 1b

Entry	TMDS (mol %)	Ti(O*i*Pr)$_4$ (mol %)	Conv.[a] (%)	Isolated yield[b,c] (%)
1	200	10	<5	–
2	500	10	<5	–
3	500	100	100	96
4	500	60	95	Nd
5	200	100	100	Nd
6	100	100	100	90

Figure 2-11 Hydrogenation of nitrile with tetramethyldisiloxane/titanium(IV) isopropoxide[53]

A concise comparison of all the above-mentioned methods for the hydrogenation of nitriles is made in Table 2-2. In the present case the required hydrogenation degree of nitrile is relatively low, so the catalyst activity for the hydrogenation should not be the main concern. Each NBR chain has more than 500 C≡Ns on average; therefore even a trace amount of secondary or tertiary amines generated may cause gel formation of NBR.

Table 2-2 Comparison of different catalysts for nitrile hydrogenation

Reduction system		**Remarks**
Heterogeneous catalysts		> 99% selectivity with additive; removal of additives
Homogeneous catalysts	Rh	~100% selectivity; no additive removal
	Ru	> 99% with addition of base; removal of additives; gel formation
	Ni	Low selectivity; gel formation
Alternative hydrogen		< 96% selectivity; removal of byproducts

2.2.4 Cross-linking in Nitrile Hydrogenation

Rubber compounds can be modified to achieve different properties through the use of different chemicals. One such property that can be both a desired outcome and a problem is an increase in strength and overall hardness of the rubber. This quality can be achieved using cross-linking in the polymer structure. This cross-linking can be manually inserted using certain chemicals, such as sulfur, that will help bind the rubber (as in the case of vulcanization), or the cross-linking can be caused by internal factors during hydrogenation. In these cases cross-linking may be a problem as it can lead to gelling of the polymer.

Regarding the mechanism of cross-linking, Zhou *et al*. stated, "The cause for the crosslink was investigated in three possibilities: (i) crosslinking caused by the hydrogenation of C≡N group; (ii) by the oxidation of C=C double bonds and (iii) by radicals in the system".[25]

A paper written by Manoj[54] researched thermally induced cross-linking in blends of PVC (Polyvinyl chloride) and HNBR. They found there was some cross-linking due to the nitrile groups with evidence of N-H and C≡N bonds in the IR spectra. They proposed that, "the mechanism of the cross-linking reaction as reported earlier is as follows: at high temperatures, PVC degrades liberating HCl. This HCl interacts with the nitrile group giving rise to amide and acid groups. At the same time, more and more reactive groups (allylic and tertiary chlorines) are formed in PVC via the degradation reaction. These reactive groups in the two phases interact to form amide and ester crosslinks". While this is not directly applicable to HNBR alone, it does show that there may be some kind of cross-linking occurring from hydrogenation of nitrile groups and that these bond formations may be caused by various chemicals, perhaps the catalyst being used in the present work. Furthermore, introducing a catalyst with a chlorine ligand (for example Wilkinson's catalyst) might form HCl with the H_2 gas, causing cross linking of this type.

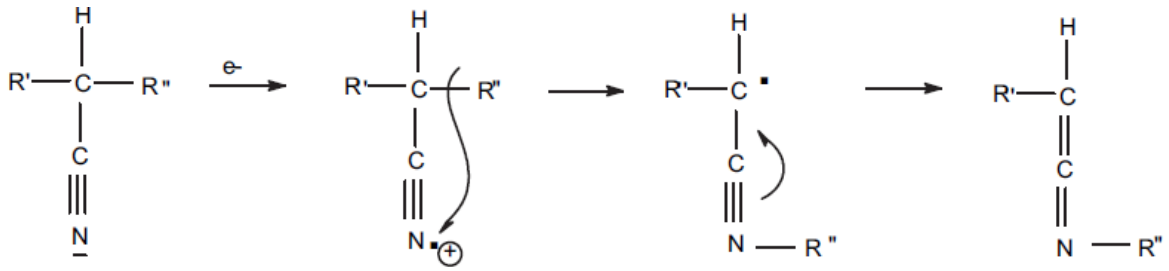


Figure 2-12 Mechanism for alkene imine formation as proposed by Perraoud *et al*.[55]

Perraud *et al*.[55] used electron beam irradiation to observe network characteristics of HNBR. It was found a chemically stable reaction forming an alkene imine function was a likely contributor to the cross-linking found in the final product. A vibration of strong intensity in the 2050-2000 cm^{-1} range was found. A possible mechanism was proposed and is shown in Figure 2-12.

2.2.5 Determination of Amines

As addressed in the beginning of section 2.2, nitrile hydrogenation is a common industrial practice for the production of amines, and will always produce secondary and tertiary amines along with the desired primary amine. So to determine what type of amine and how much of it has been produced is of great importance. Below are an introduction to the techniques and methods of determination of amines.

2.2.5.1 Titrations

Titrations are the most common method to calculate the concentration of amines in solution. It utilizes a simple procedure with readily available materials to gain a strong idea of how much amine is in solution. This method can also be easily adapted to determine the amount of nitrile in solution.[56] This method is not, however, without its drawbacks.

The main step during titration is to protonate the amine groups in solution. This is done by using either a strong or weak acid, depending on the solution composition and the amines being titrated. Perchloric acid, glacial acetic acid and hydrochloric acid are among the most commonly used titrants.[56-59] The goal of titrating the solution is to reach an equivalence point. “The equivalence point is that point during the titration when the amount of acid (or base) added is exactly equivalent to the amount of free (or bound) amine in the solution. The operator's estimate of the equivalence point is called the endpoint of the titration. The endpoint is generally determined from a change in some

property of the solution, such as pH, color, conductance, etc".[60] Once having reached an equivalence point, the volumes of solution can be used to calculate how much amine is present.

There are two types of amines found in solution, those that are "free" and those that are "bound".[60] When the acid reacts with an amine group, protonating the amine, the amine is called "bound" because it can no longer react with the acid. The amine may need to be protonated more than once before it can be considered bound. A free amine can still gain hydrogen from the acid in solution. In this way, the longer the titration takes the more bound amine is formed.

As mentioned earlier the goal is to reach the endpoint of titration. This is almost always measured using a potentiometer during titration, though there are also reports of using chemicals such as methyl violet as indicators.[58] Using a platinum catalyst and pure hydrogen it is also possible to determine the amount of nitrile in a solution by first changing the nitrile to a hydrogenated amine and then following the steps of titration.[56]

Finally, titration is not always a possible method for determining the amount of amine. Some solutions are volatile and cannot be titrated. Furthermore, titration with acid can cause inflated results in amine count, for example, "amine concentrations reported at greater than 100% of the amount added to the system, or amine concentrations from analysis not dropping in accordance with rising corrosion rates".[60] Corrosion due to acid and the acid salt may also cause problems. Determining an accurate endpoint is also difficult.

2.2.5.2 TD-GC

Thermal Desorption (TD) is a method that allows volatile organic compounds to be used more effectively in a gas chromatograph (GC). Organic compounds in the substance being sampled get trapped in a sorbent before entering the GC. The sorbent is then heated to allow release of these chemicals, but in a much smaller volume allowing higher sensitivity and smaller width of peaks in the GC analysis. The GC works just like most other chromatographic techniques where composition of the sample is determined using retention times of the column.

Taguchi *et al.*[61] described a slight variation on the standard TD-GC procedure based on "thermally assisted hydrolysis and methylation GC in the presence of an organic alkali, tetramethylammonium hydroxide". Using this new technique they were able to determine HALS (hindered amine light stabilizer) at concentrations ranging from 1000 ppm to 50,000 ppm. A separation column more polar than usual was used to prevent "undesirable adsorption of the components derived from the HALS

and to eliminate the compositional interference with those from the PP (Polypropylene) substrate." Furthermore NPD (nitrogen-phosphorus detection) was used over FID (flame ionized detection) in the final analysis steps.

2.2.5.3 Pyrolysis GC-MS

Pyrolysis refers to the use of thermal energy to chemically degrade a sample under an inert gas. The degraded sample is then pushed into the GC (gas chromatography) and MS (mass spectrometry) devices where its composition can be easily determined via retention times. Pyrolysis is required when testing polymers as polymers fragment into smaller molecules during thermal degradation. While this process does destroy the sample, very little sample is needed to be tested.[62]

Measuring HALS (hindered amine light stabilizer) additives in polymers are of significant interest. Coulier *et al*. stated, "Interestingly, no report of a successful analysis of HALS additives with liquid chromatography has been made so far. Some attempts have been made, but the polymeric structure and the presence of secondary amine-groups are thought to be the major cause of the lack of liquid chromatography methods for HALS additives".[63] Thus they studied a form of pyrolysis GC-MS instead. Their results showed a good detection system for many different HALS additives.

GC-MS is often used in polymer analysis of volatile compounds. Pyrolysis can require temperatures from 250 to 1000°C which may cause damage to the polymer and allow only relatively low mass fragments to be analyzed, though this is usually enough to define the chemistry in the original polymer.[64]

2.2.5.4 Fluorescence

Fluorescence labeling is common practice in biochemistry related fields. Specific molecules such as fluorescamine, *o*-phthaldialdehyde (OPA) and 3-mercaptopropionic acid (MPA) are used to selectively attach to amino acids.[65] These molecules are able to fluoresce when exposed to certain wavelengths of light and this fluorescence can then be measured. In this way the number of amino acids can be determined. There are some issues with interference due to natural background fluorescence, OPA-induced residual fluorescence and some ammonium signals.

Seiffert *et al*. reported using fluoresceine and rhodamine side groups as fluorescence labels in copolymers.[66] They also mentioned that, "fluorescence labels have the advantage that analytical techniques based on fluorescence are among the most sensitive methods available". These labels are

attached to polyacrylamide as described in Figure 2-13 below. In the figure, AAm = acrylamide, NAPM = *N*-(4-dimethylaminophenyl)maleimide, RITC = rhodamine isothiocyanate, FITC = fluorescein isothiocyanate.

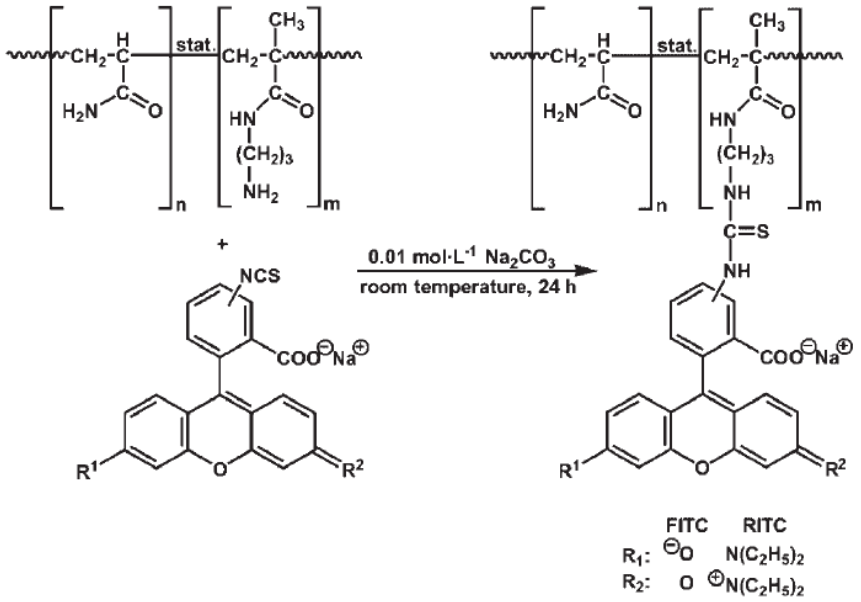


Figure 2-13 Reaction mechanism for labeling of AAm/NAPMAAm copolymers with FITC and RITC[66]

Eckstein *et al.*[67] reported using fluorescamine to determine primary amine content in polytetrahydrofuran (PTHF). It was found that water was required to hydrolyze excess fluorescamine and that "a molecular weight of 20,000 is usually the upper limit for its accuracy". It was also mentioned that the fluorescamine could only measure primary amine end groups using their proposed method. Fluorescamine is found to be highly sensitive for determining end groups of polymers, even at high molecular weights.

2.2.5.5 NMR

Ji *et al.*[68] described a way to determine primary amine composition in polymers using ^{19}F-NMR spectroscopy. The method "relies upon the clean, highly thermodynamically favourable textbook condensation reaction between a primary amine and an aryl aldehyde to form an imine (Schiff base)".

Standard NMR methods are useless in detecting amines in a polymer structure. The large polymer backbone overshadows any amine-hydrogen interactions.

The proposed method involves determining primary amine content in a wide variety of polymers including PS (polystyrene), PMMA (poly(methyl methacrylate)), PEG (polyethylene glycol), PDMS (polydimethylsiloxane), polyethers, PB (polybutylene) and polyamides.[68] This aldehyde reacts with the amine side groups to form fluorine–containing imine. This new side group can then be detected by ^{19}F-NMR and easily differentiated from other parts of the polymer. It was also mentioned that THF was not a viable solvent as it partially overlapped two of the key CF_3 resonances, making the spectra difficult to compare to a BTF (benzotrifluoride) reference. If THF must be used then a different reference would solve this issue.

2.2.5.6 Kjeldahl Method

The Kjeldahl method is often used to determine amine and nitrogen content in coal. Coal is heated with concentrated sulphuric acid.[69] A catalytic mixture is then added which converts nitrogen into ammonium sulphate. The ammonia is distilled off, absorbed in acid solution (usually boric acid or sulphuric acid) and then titrated. Variables such as heating temperature and catalyst composition play important roles in the overall accuracy and efficiency of the reaction. A mixed selenium/vanadium pentoxide catalyst is commonly used, though many different ones exist.

A new method for Kjeldahl reactions was proposed by Beet *et al*. in 1954.[70] This method uses a crystalline potassium permanganate for oxidant instead of standard oxidants. The newer method is reported to reduce reaction times significantly and also provides “an unmistakable colour indication of the completeness of conversion into ammonium sulphate”.

2.2.5.7 MALDI

MALDI (matrix-assisted laser desorption/ionization) is a special case of laser desorption Mass spectrometry that is often used in the analysis of polymers. A dilute solution of analyte polymer and concentrated matrix solution is made and then applied to a MALDI target.[64] As the solvent evaporates, the rest crystalizes and is placed in a mass spectrometer. The matrix is vaporized when a laser irradiates the target, desorbing polymer oligomers into the gas phase. The ions are then detected by analyzing their mass in the mass spectrometer. The samples must be very carefully and specifically prepared. The choice of solvent is also critical for the success of the MALDI experiment.

2.2.5.8 Near-Infrared Spectroscopy

Various absorption peaks have been noted for NH bonds. An absorption maximum around 1.5 μm is due to N-H stretching in many primary and secondary aliphatic and aromatic amines.[71] More specifically, bands 1.50-1.55 μm and 2.00-2.05 μm are stated to be primary aliphatic amines while 1.53 μm and 1.55 μm are secondary aliphatic amines.

2.2.5.9 Spectrophotometric Method

Rawat *et al*. have reported a sensitive method to determine aliphatic and aromatic primary secondary and tertiary amines.[72] A greenish violet coloured complex is formed using acetyl chloride and ferric nitrate to react with amines. Absorbance was noted at several wavelengths with maximum absorbance (plateau) at 550 nm. Some solvents interfered with the absorbance, and the absorbance is highly dependent on pH.

2.3 Vulcanization

Vulcanization is a process used on rubber so that it can acquire elastomeric properties that are useful for a variety of needs. It is achieved by forming a cross-linked network of molecules.[73] The results of vulcanization are an increase in the retractive force and a reduction in the amount of deformation that occurs.[74] The number and density of these cross-links ultimately determines the properties of the vulcanized rubber (Figure 2-14).[74,75]

The first patent for sulfur vulcanization was developed in 1839 by Charles Goodyear who noticed that metal oxides accelerated the process and improved the effect.[74] The process was slow and so, in 1906, Oenslager discovered an organic chemical accelerator in the form of aniline.[76] More accelerators were discovered over time with varying effectiveness and can be seen below in Figure 2-15. The next major achievement came when pre-vulcanization inhibitors were produced. These chemicals are added to delay the start of the vulcanization process so as to allow enough time for processing. The most common pre-vulcanization inhibitor used today is *N*-(cyclohexylthio)-phthalimide.[77]

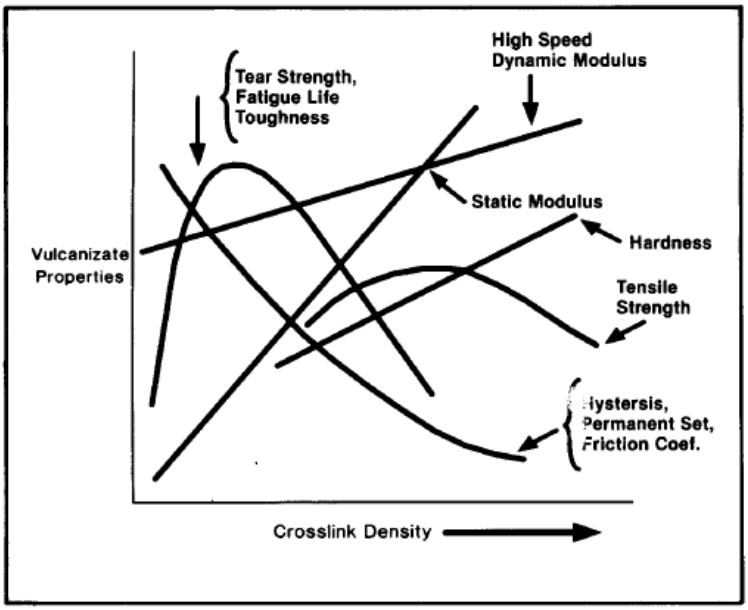


Figure 2-14 The effect of crosslink density on vulcanizate properties[74,75]

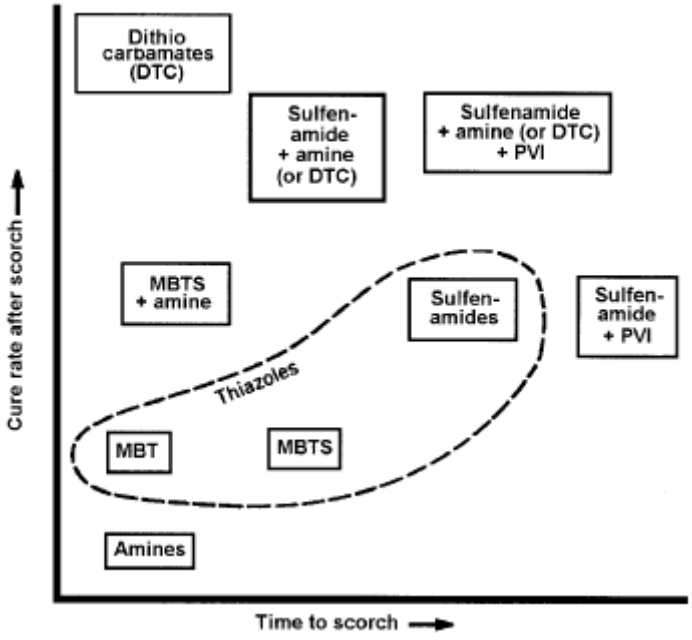


Figure 2-15 Effect of certain additives on curing time[74]

2.3.1 Types of Vulcanization

There are two main types of vulcanization employed today, sulfur and peroxide vulcanization. Sulfur vulcanization is the most commonly used type and is employed in more than 90% of all vulcanizations.[74] Sulfur vulcanization is traditionally a slow process so additives are added to speed up the process, including ZnO, stearic acid and accelerators (which act as catalysts, Figure 2-15).

Although vulcanization makes the rubber more chemically resistant, degradation and ageing still occur in the form of oxidation and ozonation.[74] Oxidation occurs through a radical-chain mechanism and is initiated by heat or light; it is slowed by adding antioxidants, such as aryl amines or phenolic compounds, which work by increasing the steric hindrance of the rubber.[74,78] Ozonation occurs due to the reaction of ozone with C=Cs, which can cause the rubber to crack. It is prevented by adding diamines during the vulcanization process which compete with ozone for the C=C sites.[74]

2.3.2 Sulfur Vulcanization

As stated above, the advantages of sulfur vulcanization are increased elasticity, increased strength and increased chemical and temperature resistance. There are, however, some disadvantages associated with the process, including safety concerns attributed to toxicity[79] of the materials used and the products formed.[80] The cold vulcanization of rubber uses carbon disulfide (a thiono-sulfur containing compound) which has been reported to cause neurological, visual and gastrointestinal effects along with nephrosclerosis, hypercortism, anemia and liver damage.[79] Additionally, hydrogen sulfide gas (H_2S) is often produced during vulcanization and is especially harmful towards human health. It can cause ocular, respiratory, neurological, cardiovascular, metabolic and reproductive effects which in some cases can lead to cancer.[81]

2.3.3 Peroxide Vulcanization

An alternative to sulfur vulcanization is peroxide vulcanization. The advantages of peroxide cross-linking are headlined by the fact that the chemicals used and produced in peroxide cross-linking are much safer to use than those applied in sulfur cross-linking. Other advantages that come with peroxide vulcanization include a simpler formulation, quicker process, good compression set and high-temperature resistance.[82,83] As can be seen in Figure 2-16, the C-C cross-link bond formed in peroxide vulcanization is stronger than the various C-S_x-C bonds formed during sulfur vulcanization; this leads to peroxide-cured rubber having better compression set and oil resistance.[83]

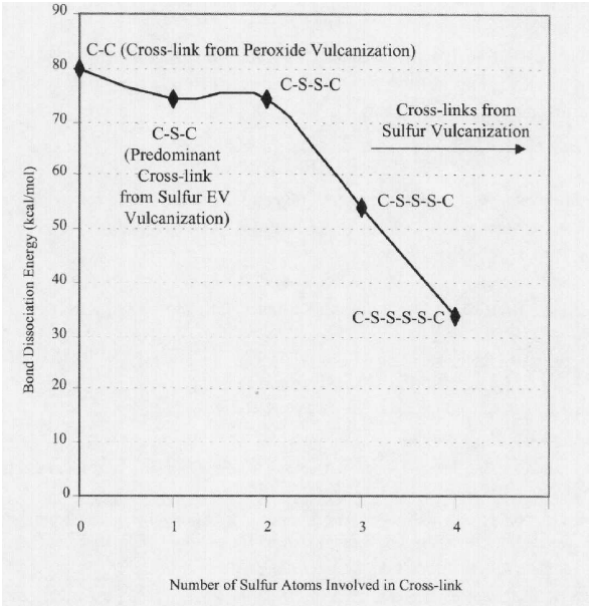


Figure 2-16 Peroxide cross-link strength versus sulfur cross-link strength[83]

One disadvantage of sulfur vulcanization studied by Gatos *et al*. has to do with the dispersion of layers in nanocomposite materials (such as rubbers or organoclays), known as intercalation.[84] They found that amine intercalants reacted with the sulfur cavities produced by the vulcanization process which results in reduced performance of the rubber. They found that peroxide vulcanization avoided this problem resulting in a rubber with superior mechanical performance.[84] Thitithammawong *et al*. studied a number of peroxides to be used in the vulcanization of epoxidized natural rubber. They tried to find a peroxide that did not produce volatile decomposition products which is a problem with peroxide vulcanization as they smell unpleasant and cause blooming, where the cross-links are only formed on the surface.[85] The reason why sulfur vulcanization is still used today is due to the fact that sulfur-cured rubber is more flexible than peroxide-cured rubber due to the sulfur cross-links; this provides sulfur-cured rubber with better tear and abrasion resistance.[83] Scorch, when the cross-links form early due to heat, is also prevalent with peroxides, whereas curing is delayed in sulfur systems minimizing scorching.[83]

Chapter 3
Objectives, Methodology and Approaches

3.1 Objectives

The aim of this research is to explore the feasibility of reducing nitrile groups in diene-based nitrile copolymers, and to discover and establish an effective catalytic system for tandem hydrogenation of both olefinic and nitrile groups in acrylonitrile butadiene rubber (NBR). The new hydrogenation process should meet the following technical demands for producing nitrile-reduced HNBR products:

a) Selectively hydrogenate nitrile groups to a certain extent within the polymer chains during the hydrogenation reaction to improve the processability and hydrophilic property of HNBR while maintaining its oil and heat resistance properties;

b) Selectively hydrogenate olefinic and nitrile groups to a certain extent within the polymer chains during the hydrogenation reaction to improve the oil and heat resistance properties and the processability and hydrophilic property of NBR;

c) The content of nitrile should be reduced at least by 10% so that the processability, hydrophilic property and oil and heat resistance properties can reach a balance;

d) Hydrogenation conversion of carbon-carbon double bond should be higher than 95%. Less than 5% of unsaturation is a threshold that ensures high-performance applications of the HNBR products;

e) No gel formation should occur or be observed in the final product in order to control the mechanical properties of the material and ensure excellent processability.

f) Optimal operation conditions should be obtained so as to keep the production cost as low as possible.

The ultimate goal of the overall project is to develop a method to hydrogenate the nitrile and olefinic groups of NBR as well as perform environmentally friendly vulcanization all in one step.

3.2 Experimental

In this section, only general investigation methods, experimental procedures, and characterization methods used for the research work will be presented. Detailed information of specific chemicals and modified experimental processes will be found in subsequent chapters. The approach strategies for this research are also introduced here.

3.2.1 Materials

All the chemicals were used as received. Nitrile rubber (Perbunan T3429 and T3435) containing about 34 wt% acrylonitrile unit was obtained from Lanxess Inc. (Germany). Nitrile butadiene rubber latex (Perbunan latex, 15 g polymer solid per 100 ml of latex) was also provided by Lanxess Inc. Other chemicals are listed in Table 3-1.

Table 3-1 List of chemicals

Chemical	Grade	Supplier
Acetone	Reagant	UW Chem-Store
Argon $_{(g)}$	Ultra High Purity 5.0	Praxair
Benzene, deuterated ($C_6D_{6)}$	99.5%	Cambridge Isotope Laboratories
Ethanol	HPLC, 91%	Fisher Scientific
$H_{2\,(g)}$	Ultra High Purity 5.0	Praxair
Hexane	Anhydrous, 95%	Sigma-Aldrich
HNBR	Therban 3446	Lanxess
Methyl ethyl ketone (2-butanone)	Certified ACS, 99.9%	Fisher Scientific
Monochlorobenzene	Reagent, 99%	Sigma-Aldrich
Na/Hg amalgam	5%	Sigma-Aldrich
NBR	Perbunan T3435	Lanxess
$N_{2\ (g)}$	Ultra High Purity 5.0	Praxair
PBz_3	98%	Sigma-Aldrich
$P(i\text{-}Pr)_3$	98%	VWR
Propan-2-ol	HPLC, 99.9%	Sigma-Aldrich
$P(t\text{-}Bu)_3$	98%	Sigma-Aldrich
$[RhCl(C_2H_4)_2]_2$		Sigma-Aldrich
$RhCl(PPh_3)_3$ (Wilkinson's catalyst)	11.10 wt% Rh	Lanxess
Rhodium(III) chloride hydrate	38.5 wt% Rh	Sigma-Aldrich, Lanxess
SBR	BUNA VSL 5025-0 HM	Lanxess
THF	Reagent, >99%	Caledon
THF	HPLC, $\geq$ 99.9%	Sigma-Aldrich
Toluene	ACS, >99.5%	Fisher Scientific
Toluene-d_8	99.6%	Cambridge Isotope Laboratories
Triphenylphosphine (TPP)	99%	Sigma-Aldrich

3.2.2 Equipment

The main equipment used in this work includes: a Parr 4560 Mini Bench Top Reactor (300 mL) equipped with Parr 4842 Controller; Bio-Rad Excalibur 300MXPC Fourier Transform Infrared Spectroscopy (FT-IR); Thermo Nicolet 6700 Fourier Transform Infrared Spectroscopy operated with OMNIC software; Thermo HAAKE MARS II Rheometer operated with RheoWin Software and equipped with cone/plate sensors and Pressure Sensor D400/300 (with PZ38b Rotor); TA Instruments AR2000 Rotational Rheometer equipped with cone/plate sensors; Malvern Viscotek GPCmax VE 2001 Gel Permeation Chromatography (GPC) moduled with TDA 305 Triple Detector Array and UV detector 2500. A column set was employed consisting of three 300×8 mm columns filled with a PL (polyhydroxyl) gel with an average particle size of 10 μm.; Microtrac Nanotrac NPA250 particle size analyzer (Dynamic Light Scattering or DLS); Vacuum Atmospheres Company (VAC) HE493 Dri-Train glove box; Vacuum Atmospheres Company (VAC) Nexus One glove box; Ohaus Analytical Plus Balance AP250D (resolution of 0.01 mg) and Sartorius Laboratory LC3200D; Bruker 300 MHz Nuclear Magnetic Resonance (NMR) equipped with QNP Probe device.

3.2.3 Characterization

In order to determine the conversion of carbon-carbon double bonds and carbon-nitrogen triple bonds in the hydrogenation reaction, samples were taken at certain time intervals during the experiments. A Bio-Rad FTS 3000MX spectrometer and a Thermo Nicolet 6700 spectrometer were used for Fourier transform infrared (FT-IR) analysis of samples. The degree of hydrogenation was calculated based on the peak strength from the IR spectra according to American Standard Test Method (ASTM) D5670-95. For FT-IR analysis, the latex samples were coagulated with ethanol to yield dry solid rubber which will then be dissolved in MEK. Afterwards, the MEK solution was spread on NaCl disk and dried to form a rubber film for measurement. Each sample was tested twice and the average value was taken. In fact, latex samples may also be prepared by directly casting the latex on NaCl disks and drying to obtain a film for FT-IR scans. For solution measurements (e.g. nitrile hydrogenation and SBR hydrogenation), liquid samples were casted as rubber films on a NaCl disk, and analysed through FT-IR analysis. IR spectra were collected using a Bio-Rad Excalibur 300MXPC spectrometer or a Thermo Scientific Nicolet 6700 spectrometer. These data would be analyzed at three wave-number regions as shown in Table 3-2, and from these peaks the progression of selective hydrogenation would be calculated. Without undergoing any hydrogenation of carbon-carbon double bonds, the content of C≡N in both HNBR and NBR is approximately 40% which remains unchanged

during the olefinic hydrogenation experiments. The calculation for C=C hydrogenation can be found below:[86]

$$A723 = absorbance\ at\ 723\ cm^{-1}$$
$$A970 = absorbance\ at\ 970\ cm^{-1}$$
$$A2236 = absorbance\ at\ 2236\ cm^{-1}$$

$$A(723) = \frac{A723}{A2236}\ and\ A(970) = \frac{A970}{A2236}$$

$$K(723) = 0.255, a\ constant\ specific\ to\ this\ peak$$
$$K(970) = 2.3, a\ constant\ specific\ to\ this\ peak$$

$$F = 1 + \frac{A(970)}{K(970)} + \frac{A(723)}{K(723)}$$

$$C(BR) = \frac{A(970)}{[K(970) \times F]} = carbon - carbon\ double\ bonds\ remaining\ in\ HNBR$$

$$C(HBR) = \frac{A(723)}{[K(723) \times F]} = methylene\ groups\ formed\ from\ hydrogenation\ of\ NBR$$

$$\boldsymbol{Degree\ of\ Hydrogenation}\ (\boldsymbol{mol}\ \%) = 100 - \frac{C(BR)}{C(BR) + C(HBR)} \times 100$$

To determine the conversion of nitrile groups, a similar method has been used as in the hydrogenation of the olefinic groups. However, it should be noted that the content of carbon-nitrogen bonds, which is the internal standard, decreases in the hydrogenation of nitrile groups, while it remains unchanged in the hydrogenation of carbon-carbon double bonds. This difference will definitely affect the accuracy of the results of conversion of nitrile groups. Being aware of this fact, some work was carried out to verify the error between the calculated values and actual values, which will be discussed as follow. To do this, HNBR was used in the experiments as little (< 5%) carbon-carbon double bonds exist in it; in other words, the peak at 723 cm^{-1} (-$(CH_2)_X$-) in the IR spectra remains unchanged. So the peak at 723 cm^{-1} is used as an internal standard, and the ratio of the peak value (peak height) of the nitrile group (at wavenumber 2236 cm^{-1}) and peak height at 723 cm^{-1} is calculated for each sample which is taken during the reaction. In the end, a series of values of the ratio is listed.

It was found that the ratio decreases as the reaction proceeds, which means that the nitrile content is being reduced, and the error is less than 5% which is acceptable. As there is no more efficient or accurate method published to calculate the nitrile content or amine content in macromolecule polymers, the method mentioned above has been accepted and used.

Table 3-2 Characteristic peaks in FT-IR spectra of NBR and HNBR[87-89]

Wavenumber (cm^{-1}**)**	**Functional Group**	**Remark**
2236 cm^{-1}	-C≡N	Decreases when hydrogenated
970 cm^{-1}	-CH=CH- (backbone)	Decreases, only present in NBR
723 cm^{-1}	$-(CH_2)_X-$ where x>4	Increases as backbone is hydrogenated

Gel formation (gelling or gelation) was determined by checking if the resultant HNBR was totally soluble in MCB, MEK or THF at room temperature by the naked eye. It can be also confirmed via viscosity using a Thermo HAAKE MARS II Modular Advanced Rheometer System equipped with Pressure Sensor D400/300 (with PZ38b Rotor). Once gel was found, the gel content can be checked for some samples according to ASTM D3616-95 method.

The particle size distribution of the latex, before and after hydrogenation, was determined at room temperature using a Nanotrac NPA 250 particle size analyzer (Microtrac Inc.) based on dynamic light scattering measurement principles.

Two other methods were also used to characterize the materials in this project. NMR was performed on a Bruker 300 MHz with QNP Probe device and was used to characterize catalysts based on ^{1}H-NMR (proton NMR) and ^{31}P-NMR (phosphorous NMR). Gel Permeation Chromatography (GPC) was used to determine the molecular weight of SBR solutions based on refractive index. Viscotek's GPC Max: VE 2001. UV Detector 2500 and Triple Detector Array 305 were used in combination to measure the data.

3.2.4 Hydrogenation Procedure

The experimental procedure used to study the selective hydrogenation of nitrile rubbers remains unchanged most of the time. Solutions of NBR or HNBR (2.5-15 wt%) in tetrahydrofuran (THF) were initially prepared and placed on a shaker for one day to allow for the complete dissolution of rubber.

Hydrogenation of NBR and HNBR samples was performed in a Parr 4560 Mini Bench Top Reactor (300 mL) equipped with a Parr 4842 Controller. A designated amount of desired rubber solution was

added to the reaction vessel. The reactor was then bolted shut after assembling all parts and tested for leaks with 100 psig H_2 gas. Once the reactor was assembled and tested for leaks, the vessel was degassed using H_2 gas. To degas the reactor, the reaction vessel was placed in an ice/water mixture and the gas output valve was connected to a hose placed in a bucket of water. With all valves closed the reactor was turned on to rotate at 250 rpm. Open H_2 inlet valve and fill the reactor vessel with 100 psig H_2 gas, then close the hydrogen inlet valve and open the gas output valve to allow H_2 slowly leak out of the output hose causing a trail of small bubbles in the bucket of water.

Once the pressure in the reactor was at 0 psig and bubbles stopped flowing, the H_2 input valve was opened slightly while the output valve into the water bucket was fully opened. The reactor was kept this way for at least 30 min as H_2 was allowed to flow in and out of the reaction vessel. Once the time was up, both valves were quickly closed, and the ice/water mixture was removed and the vessel was dried. The heating mantle for the reactor was placed over the vessel and the heater was adjusted to set the reaction temperature.

While the reaction vessel was reaching the desired temperature, a designated amount of catalyst was prepared in a glove box. The catalyst was obtained using a gas-tight syringe under an argon atmosphere. Once the desired temperature was reached the gas exhaust valve was quickly opened to release pressure built up during heating. The catalyst was quickly taken from the argon environment and inserted into the reactor through a valve. All valves were closed, temperature was increased if desired and the pressure was increased to a certain value, usually 500-1000 psig H_2. Samples were taken normally every hour for 5 to 6 hours and measured on sodium chloride disks via FT-IR.

For each experiment, many repeated tested have been conducted to confirm the consistency and accuracy, and the results match very well and the error is within 5%.

Chapter 4

Hydrogenation of Acrylonitrile Butadiene Rubber (NBR) in Latex Form Using Rhodium(III) Chloride

4.1 Introduction

Since its inception, Wilkinson's catalyst, $RhCl(PPh_3)_3$, has been widely used for the hydrogenation of olefinic double bonds in diene-based polymers and is until this time considered to be the most preferable one. It has been reported that Wilkinson's catalyst has excellent performance for hydrogenation of NBR in solution form and latex form, and the technology for solution hydrogenation of NBR has already been successfully commercialized many years ago[1,90-92]. It should also be noted that triphenylphosphine (TPP), the ligand of Wilkinson's catalyst, is always employed in the hydrogenation experiments catalyzed by Wilkinson's catalyst as it facilitates the transport of $RhCl(PPh_3)_3$ into polymer particles in latex form[90,93]. In fact, the reactivity of Wilkinson's catalyst in NBR latex hydrogenation is significantly lower than that in solution form due to its insolubility in water and insufficient contact with rubber particles (the substrate)[89]. As a result, the main goal of this study was to improve the dispersion of $RhCl(PPh_3)_3$ in the aqueous phase and provide a high conversion of carbon-carbon double bonds in the NBR latex.

The traditional synthetic procedure of Wilkinson's catalyst $RhCl(PPh_3)_3$ is to reflux $RhCl_3 \cdot 3H_2O$ and recrystallized TPP in ethanol[94,95], where rhodium chloride ($RhCl_3$), a highly water-soluble compound, is one of the most common precursors to synthesize the rhodium complex.[96,97] Since NBR latex is an aqueous system, it would be preferable to prepare $RhCl(PPh_3)_3$ *in situ* from the precursor and the ligand of the catalytic system. Therefore, the investigation on direct *in situ* synthesis of Wilkinson's catalyst and olefin hydrogenation in NBR latex was initiated.

4.2 Experimental

4.2.1 Materials

Nitrile butadiene rubber latex: The commercial NBR latex (Perbunan latex, 15 g polymer solid per 100 ml of latex) used in this investigation was provided by Lanxess Inc.

Solvent: ethanol, toluene, monochlorobenzene (MCB) and methyl ethyl ketone (MEK) were all purchased from Fisher Scientific Ltd. All solvents were used as received.

Hydrogen gas and nitrogen gas used for the hydrogenation studies were oxygen-free with ultra high 99.999% purity provided by Praxair Inc.

Catalyst and co-catalyst: Wilkinson's catalyst, $RhCl_3$ (rhodium chloride) and triphenylphosphine (TPP) were obtained from Lanxess Inc.

4.2.2 Hydrogenation Procedure

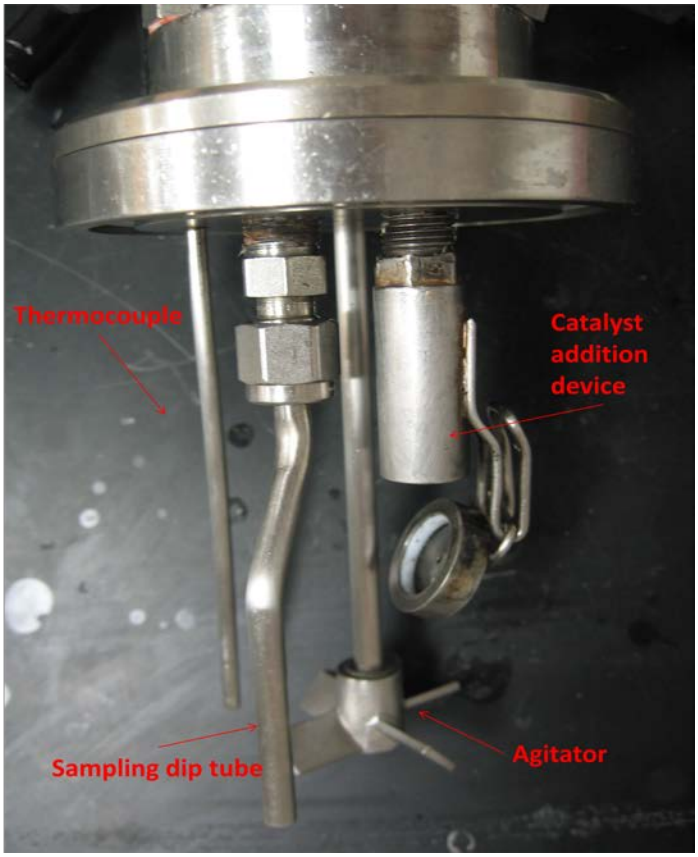


Figure 4-1 Configuration of the head of a customized 300 mL Parr autoclave

The hydrogenation experiments were carried out in a 300 mL autoclave manufactured by Parr Instruments. NBR latex and TPP were mixed in the reactor vessel. Rhodium chloride, the precursor, was added in a tiny glass bucket (wall thickness is less than 0.2 mm) and then carefully placed in a catalyst addition device attached to the head of the reactor (Figure 4-1). The head of the reactor must be kept straight all the time to prevent the bucket (which is filled with rhodium chloride) from falling or spilling. Total volume of the NBR latex is 100 mL in most cases. The mixture of solution was degassed with nitrogen or argon gas for at least 30 minutes and then heated up to the desired temperature. After that, the catalyst precursor was charged into the mixture with hydrogen gas (100 psig), and hydrogen pressure was increased to the desired level. The hydrogen pressure and reaction temperature remained constant throughout the entire experiment. Samples were taken at regular intervals and measured by FT-IR. A more detailed procedure is provided in Chapter 3.

4.2.3 Characterization

The conversion of carbon-carbon double bonds (hydrogenation degree) of NBR latex was determined by FT-IR and confirmed by ^{1}H-NMR. In FT-IR analysis, the polymer in the latex was precipitated by slowly dripping ethanol into the latex sample under uniform agitation. After the solvent was decanted, the precipitated rubber was washed with water and dried under vacuum. The dried solid rubber was re-dissolved in methyl ethyl ketone (MEK) and the solution was cast onto a sodium chloride crystal disc. The NaCl disk was dried and a polymer film formed on it before it is ready for FT-IR analysis. The degree of hydrogenation was calculated from the FT-IR spectra according to the peak intensity. The detailed method is described in section 3.2.3.

Average molecular weights (Mn and Mw) and the molecular weight distribution were determined using a Malvern Viscotek gel permeation chromatography (GPC) with THF as the mobile phase. The GPC system has a low angle laser light scattering (LALLS) and right angle laser light scattering (RALLS) set, and is also equipped with a Refractive Index (RI) detector, Viscometer and UV (ultra-violet) detectors. A column set was employed consisting of three 300×8 mm columns filled with a PL gel with an average particle size of 10 μm.

The dynamic viscosity of the NBR latex and its hydrogenated product were determined using a Thermo HAAKE II rotational rheometer. The morphology of the NBR latex particles is determined using a dynamic light scattering (DLS) particle size analyzer. Detailed information of the equipment is listed in section 3.2.2.

4.3 Results and Discussion

4.3.1 Effect of Tripheylphosphine (TPP) on NBR Latex Hydrogenation

Hydrogenation of a macromolecular material, like polymers with high molecular weight, is different from that of small molecules, especially in an aqueous/organic biphasic system like NBR latex. The polymer chains coil and entangle in the polymer particles and do not have much room to move. A similar thing happens to the carbon-carbon double bonds within the polymer chains.[98] As a result, the diffusion or transport of the catalyst is of great importance in the whole process. Generally speaking, there are three possible places that catalyst exists: the aqueous phase, the interfacial phase of water and polymer particles and the interior of the polymer particles. It is also known that most of the catalyst will start with the hydrogenation of the carbon-carbon double bonds on the surface of the polymer particles first before penetrating deeper into the polymer particle.[99] Therefore, improvement of the diffusion of catalyst into the polymer particle is the main issue.

From solution hydrogenation studies, it is known that the addition of TPP as a co-catalyst ligand with Wilkinson's catalyst is necessary to maintain high catalytic activity.[93] Previous work by our research group[89] has shown that the most important role of TPP in the hydrogenation of NBR latex using Wilkinson's catalyst is its function as a "catalyst mass transfer promoter". That is to say, Wilkinson's catalyst dissolves in the melted TPP phase at 130^{o}C (the melting point of TPP is around 80^{o}C), and then the catalyst was brought into the polymer particles by the liquid TPP droplets, because the hydrophobic liquid TPP tends to associate with the polymer particle phase.

In the latex hydrogenation catalyzed by using $RhCl_3$, without any TPP added in the system, gel formation occurs very quickly. As previously stated, Wilkinson's catalyst is prepared by refluxing $RhCl_3 \cdot 3H_2O$ with recrystallised TPP in ethanol where TPP is the reducing agent. In the experiments of the present study, Wilkinson's catalyst is synthesized *in situ*, which explains why gel formation occurs when no TPP is added. So the catalyst should be defined as $RhCl_3$/TPP. Furthermore, an excess of TPP acts as a reducing agent for the Rh(III) species. The possible gel formation was alleviated since Rh(III) was transformed into Wilkinson's catalyst in the presence of TPP.

It is clearly shown in Figure 4-2 that the latex hydrogenation with recrystallised TPP and the one with original TPP yield similar results. However the one using regular TPP results in micro-gel formation while the other one does not, which confirms the present finding that recrystallised TPP provides

better dispersion in the system and the transfer of the catalyst into particles occurs more easily and efficiently.

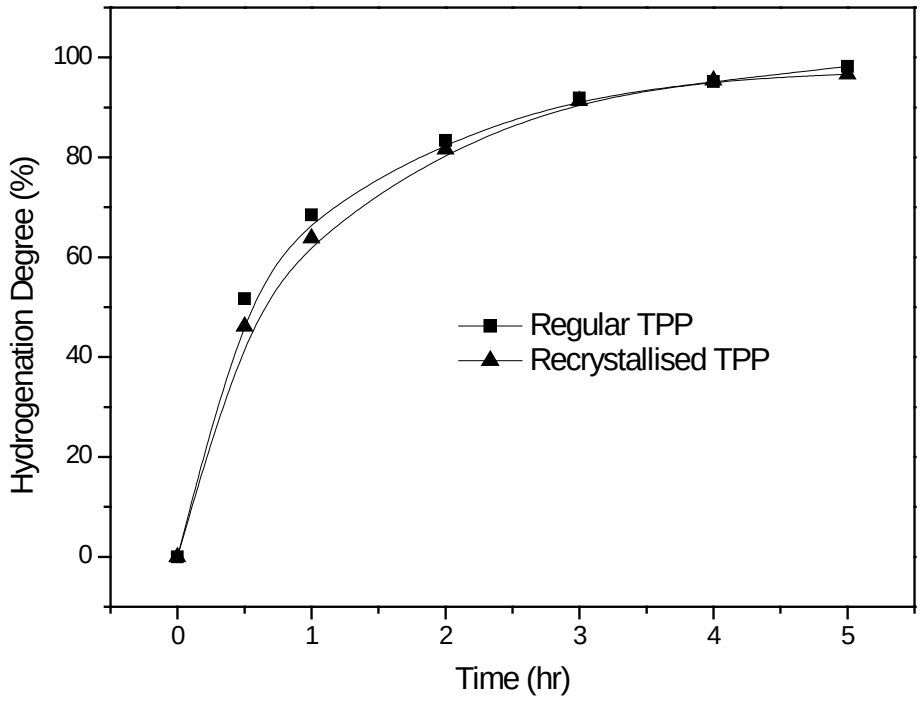


Figure 4-2 Effect of TPP on NBR latex hydrogenation

Perbunan latex F42-184/05 (15 g rubber solid/100 ml) = 25 ml; water = 75 ml; TPP/rubber = 10 wt%; Rh/rubber = 1.0 wt%; 600 rpm; 160^{o}C; H_2 = 1000 psig; time for *in situ* synthesis at 100^{o}C = 90 min

Moreover, the effect of different amounts of TPP was also carried out, which is shown in Table 4-1. Adding more TPP significantly improves the catalyst's performance (#1, #4, #5 in Table 4-1); the reaction time was reduced from almost a day to only 5 hours. It seems that as long as the TPP/catalyst ratio is over 10 wt% (TPP/Rh is 10mol/mol), the rate of latex hydrogenation is only slightly affected by the amount of TPP. The reason is that excessive TPP may shift the equilibrium of the dissociation of Wilkinson's catalyst and inhibit its reactivity.[93] Therefore, the added TPP to catalyst ratio was set at 10 wt% (TPP/Rh is 10mol/mol) for all the experiments.

Table 4-1 Effect of different amounts of TPP on NBR latex hydrogenation

#	$RhCl_3 \cdot 3H_2O$ (mmol)	TPP (mmol)	TPP/Rh (mol/mol)	Temperature (^oC)	Time (hr)	Hydrogenation Degree (mol)
1	0.143	1.43	10	160	5	98%
2	0.143	2.86	20	160	5	96%
3	0.143	7.13	50	160	5	98%
4	0.143	0.71	5	160	8	96%
5	0.143	0.143	1	160	22	95%

Note: NBR latex = 100 mL (30 g/L); H_2 = 1000 psig

4.3.2 Effect of Temperature on NBR Latex Hydrogenation

The results of NBR latex hydrogenation under different temperatures are shown in Figure 4-3. The hydrogenation reaction was studied from 130^{o}C to 180^{o}C at a constant reaction pressure and catalyst concentration. It clearly shows that the reaction rate of hydrogenation significantly increases with increasing temperature, indicating that the reactivity of the catalyst is increased on increasing the temperature. It is obvious that a high temperature induces faster movement of the molecules, but another important reason is that the transport of the catalyst from the aqueous phase into the polymer particles has been accelerated due to increasing solubility of TPP. 160^{o}C was found to be the optimal reaction temperature, and 95% conversion of NBR to HNBR was achieved within 5 hours.

Besides, hydrogenation experiments at 165^{o}C, 170^{o}C and 175^{o}C were also conducted but not shown in Figure 4-3 due to similar results; and at 180^{o}C or more, there was no further increase in the reaction rate. This result possibly resulted from a decomposition of the complex at higher temperatures. When the Parr reactor was opened, there was already a lot of precipitated rubber which was very dark and hard. The results are consistent with previous research that the optimal reaction temperature for latex hydrogenation using Wilkinson's catalyst is between 150^{o}C and 170^{o}C. Due to Zhenli Wei's work,[89] it was found that a linear response can be observed over the range of 152^{o}C-170^{o}C using Wilkinson's catalyst and the activation energy is determined to be 57.0 kJ/mol. Therefore, it is concluded that temperature plays a very important role in the hydrogenation reaction. Temperature could affect both the activity and stability of the catalyst.

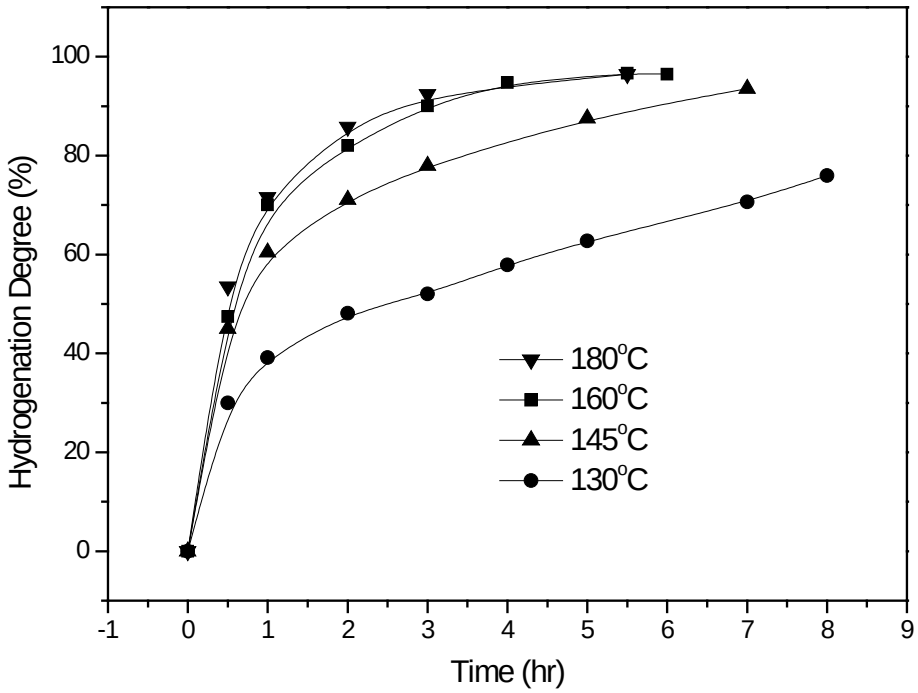


Figure 4-3 Effect of temperature on hydrogenation of NBR latex using $RhCl_3$

Perbunan latex F42-184/05 (15 g rubber solid/100 ml) = 25 ml; water = 75 ml; TPP/rubber = 10 wt%; catalyst/rubber = 1.0 wt%; 600 rpm; 160°C; H_2 = 1000 psig

4.3.3 Effect of Agitation Speed on NBR Latex Hydrogenation

Changing the rotational speed of the agitator is often a standard technique used to study the influence of external mass-transfer resistance (the gas-liquid transport resistance). Agitation speeds of 0 rpm to 600 rpm have been studied. Figure 4-4 shows that all curves coincided very well and the degree of hydrogenation are all around 81% after 5 h. However, there are some differences in the curves for samples taken during the first hour. During this period, the degree of hydrogenation decreased when the agitation speed was decreased, probably since the catalyst and TPP did not disperse evenly at the beginning due to the low agitation speed.

After 1 hour, the whole system became much better dispersed, and then the agitation speed difference is not as distinctive as before. This emphasizes why similar results were obtained at 5 hr. It is

concluded that the gas-liquid transport does not affect the performance of latex hydrogenation using $RhCl_3$/TPP very much, which is saying that on the other hand, internal mass transfer is of major importance in latex hydrogenation using $RhCl_3$/TPP.

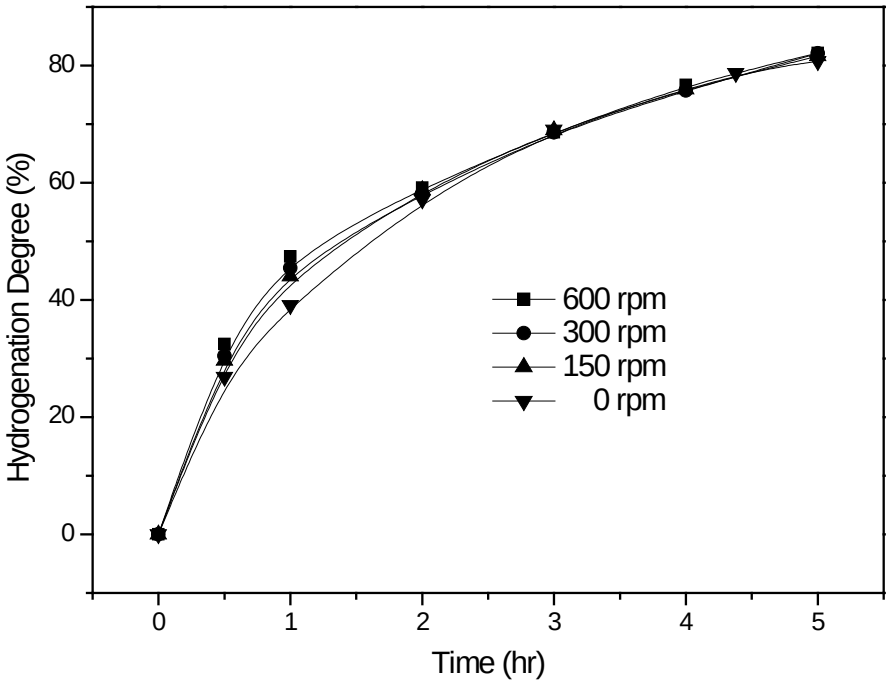


Figure 4-4 Effect of agitation speed on hydrogenation of Perbunan latexes using $RhCl_3$

Perbunan latex F42-184/05 = 25 ml; water = 75 ml; catalyst/rubber = 0.3 wt%; TPP/rubber = 10 wt%; 160^{o}C; H_2 = 900 psig

4.3.4 Effect of H_2 Pressure on NBR Latex Hydrogenation

The influence of hydrogen pressure on the latex hydrogenation reaction was examined. Figure 4-5 shows that the degree of hydrogenation drops as the hydrogen pressure is decreased. It seems that H_2 pressure does have some effect on latex hydrogenation using $RhCl_3$/TPP, because higher H_2 pressure results in higher concentration of H_2 in the aqueous phase which causes the hydrogenation to proceed faster. However, the decrease of conversion dropped slightly from 96% to 90%. It may be concluded

that the hydrogenation rate is mainly controlled by the catalyst mass transfer within the latex particles.

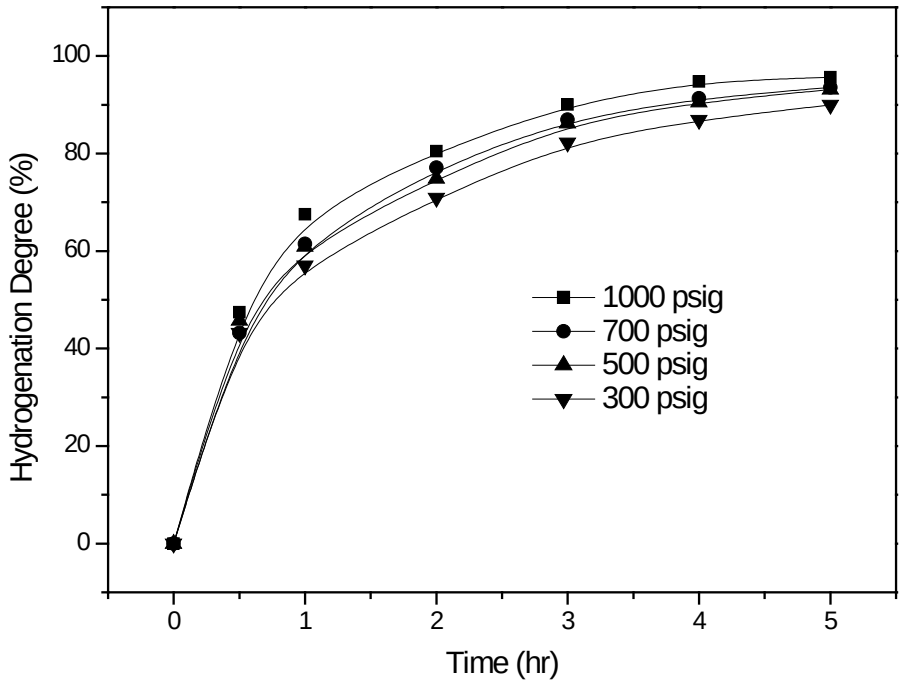


Figure 4-5 Effect of H_2 pressure on hydrogenation of Perbunan latex using $RhCl_3$

Perbunan latex F42-184/05 (15 g rubber solid/100 ml) = 25 ml; water = 75 ml; TPP/rubber = 10 wt%; catalyst/rubber = 1.0 wt%; 600 rpm; 160^{o}C

4.3.5 Effect of Rhodium/Rubber Ratio on NBR Latex Hydrogenation

From the results, it can be concluded that the catalyst/rubber ratio plays an important role in NBR latex hydrogenation. The amount of catalyst has a major effect on the degree of hydrogenation. From Figure 4-6, it can be seen that the degree of hydrogenation decreased as the catalyst/rubber ratio decreased. Another phenomenon is that, when the catalyst/rubber ratio is low, less cross-linking of the polymer is observed, so the residual $RhCl_3$ may cause the gel formation. When the catalyst/rubber ratio is 0.8 wt%, the results were almost the same as for the hydrogenation with a catalyst/rubber ratio

of 1.0 wt%, which means it is harder or impossible for excess rhodium chloride to be coordinated with TPP and be transported into the polymer particles.

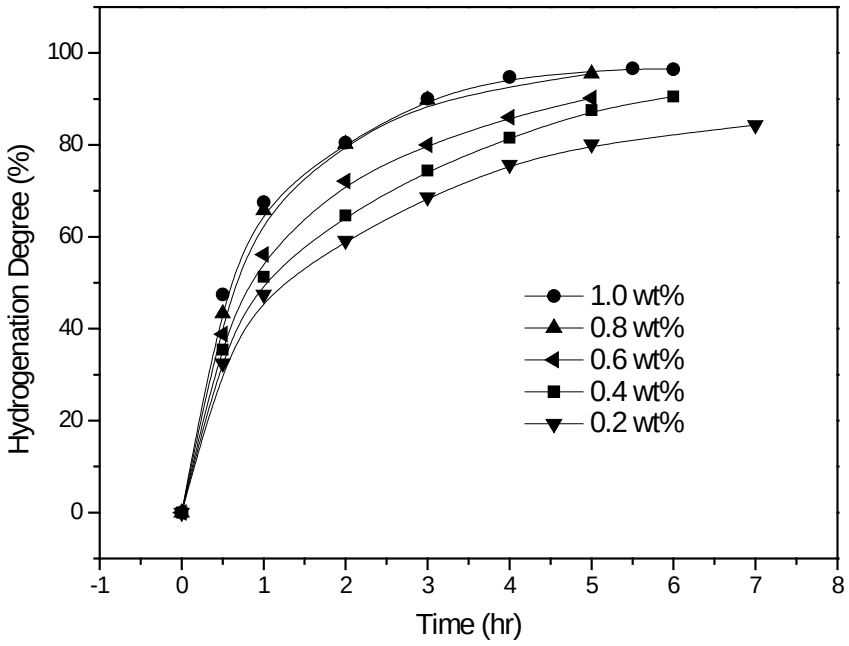


Figure 4-6 Effect of catalyst/rubber ratio on the hydrogenation of NBR latex using $RhCl_3$

Perbunan latex F42-184/05 = 25 ml; water = 75 ml; TPP/rubber = 10 wt%; 600 rpm; 160°C; H_2 = 1000 psig

Again, it is worth noting that the product tends to be more cross-linked when adding more catalyst and the $RhCl_3$ salt seems to be related with the onset of cross-linking. The biggest problem in the *in situ* catalyst synthesis process is the cross-linking in the final product. Unfortunately, the mechanism of cross-linking is still unclear. Singha[100] reported that $RhCl_3 \cdot 3H_2O$ caused gel formation when it was added to the NBR latex at 75°C and 1 atmosphere of N_2, which is confirmed by previous results in this work. However, in the presence of TPP, no gel or little gel was observed in the final product, which is probably due to the fact that Wilkinson's catalyst could be synthesized *in situ* from $RhCl_3$ and TPP during the reaction, and it is a well-known fact that Wilkinson's catalyst does not cause gel formation during NBR latex hydrogenation. The cross-linking encountered is probably caused by the

excess $RhCl_3$ in the *in situ* synthesis of Wilkinson's catalyst. So the more Wilkinson's catalyst could be synthesized *in situ* from $RhCl_3$ and TPP, the less the amount of gel would be formed. In order to solve this problem, a longer period of heating time might be helpful for *in situ* synthesis of Wilkinson's catalyst.

4.3.6 Effect of *in situ* Synthesis of Wilkinson's Catalyst on NBR Latex Hydrogenation

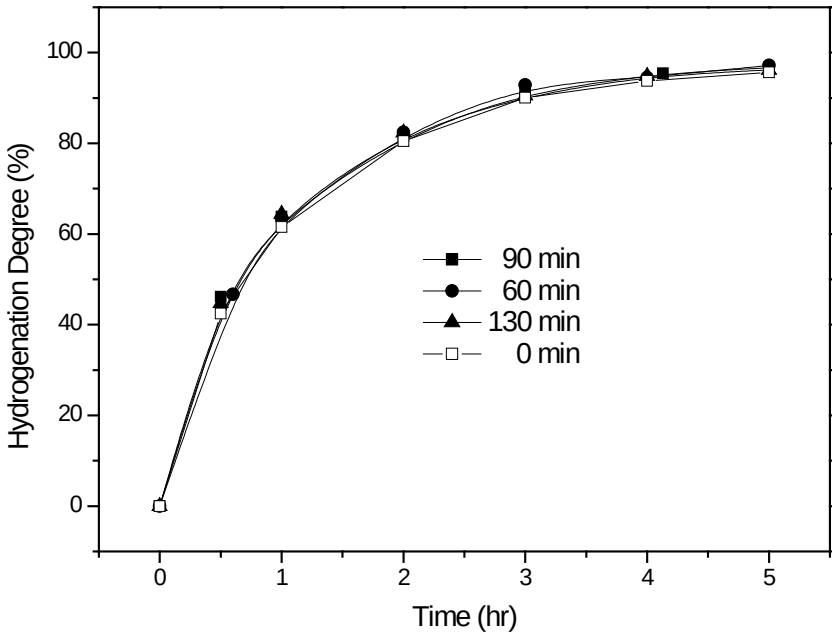


Figure 4-7 Effect of duration of *in situ* synthesis of Wilkinson's catalyst

Perbunan latex F42-184/05 (15 g rubber solid/100 ml) = 25 ml; water = 75 ml; TPP/rubber = 10 wt%; catalyst/rubber = 1.0 wt%; 600 rpm; 160^{o}C; H_2 = 1000 psig; heating time at 100^{o}C before *in situ* synthesis = 90 min

In order to increase the yield of *in situ* synthesis of Wilkinson's catalyst and to deliver more catalyst into polymer particles, a certain amount of heating time is given to the *in situ* synthetic process of Wilkinson's catalyst. Figure 4-7 shows that extra heating time slightly improves the hydrogenation reaction, which means a little more $RhCl_3$ transforms into Wilkinson's catalyst. However, on increasing the heating time from 60 min to more than 2 hours, no large increase is observed. The results also show that the final product of the hydrogenation experiment which has a certain time of

heating tends to be dissolved in MEK faster that the ones produced by the normal procedure, indicating that less gel or micro gel formed. So a heating time for *in situ* synthesis is necessary to avoid the cross-linking problem. As previously discussed, in latex hydrogenation using $RhCl_3$/TPP the catalyst is synthesized *in situ* and the results show that 60-90 min is the optimal heating time for *in situ* synthesis.

4.3.7 Hydrogenation of NBR Latex with Addition of Ethanol as Co-solvent

Cross-linking problems have always been the major issue in polymer hydrogenation and residual metal catalysts are one of the main causes. As reported by Osborn,[94] Wilkinson's catalyst is prepared by refluxing $RhCl_3 \cdot 3H_2O$ with recrystallised TPP in ethanol. Ethanol is a good solvent for TPP, so addition of ethanol may improve the *in situ* synthesis of Wilkinson's catalyst. Figure 4-8 shows the results and following conclusion can be drawn. When the catalyst/rubber ratio is 0.5 wt% (maybe higher), adding ethanol (15 ml) does not increase the degree of hydrogenation; when the catalyst/rubber ratio is 0.3 wt%, adding ethanol (15 ml) can improve the performance of $RhCl_3$ considerably. The degree of hydrogenation is increased from 80% to ~90% after 5h.

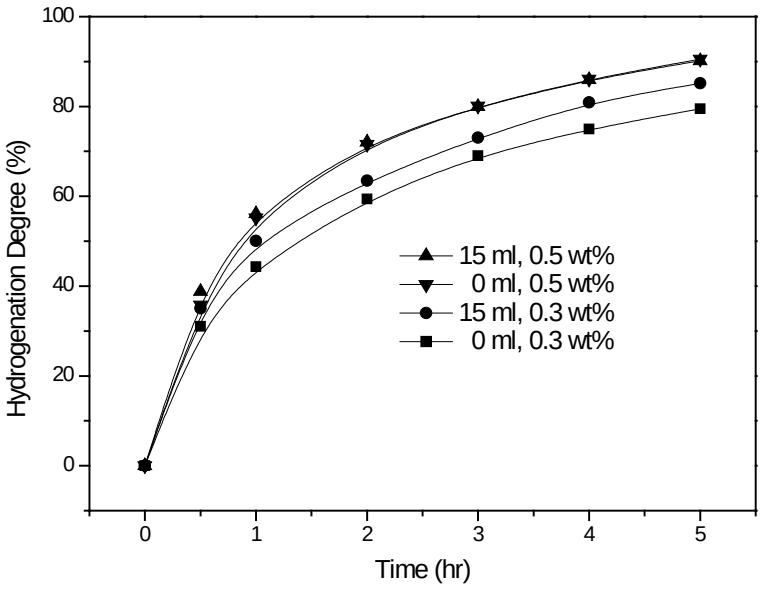


Figure 4-8 Hydrogenation of Perbunan latex using $RhCl_3$ with ethanol as co-solvent

Perbunan latex F42-184/05 = 25 ml; water = 75 ml; TPP/rubber = 10 wt%; 600rpm; 160°C; H_2 = 1000 psig

In latex hydrogenation using $RhCl_3$/TPP, Wilkinson's catalyst is synthesized *in situ*. So ethanol provides an excellent media for *in situ* synthesis and more Rh is transformed to Wilkinson's catalyst. Also, before *in situ* synthesis, TPP can be melted in ethanol and well dispersed in the system. Furthermore, during the hydrogenation process, TPP which is dissolved in ethanol can provide better transfer of catalyst into particles. According to our previous work, there is no gel formation in the latex hydrogenation using Wilkinson's catalyst; the results in this study show that HNBR produced by this method is dissolved in MEK very fast, without any shaking required. Therefore, the effect of ethanol could be summarized as increasing the reaction rate and decreasing the cross-linking in the final product. One thing that worth to note is that, ethanol serves as the co-solvent of $RhCl_3$, not the solvent of NBR latex, so this catalytic NBR latex hydrogenation system is 100% solvent-free.

4.3.8 Cross-linking in NBR Latex Hydrogenation

As previously discussed, the mechanism for cross-linking in NBR hydrogenation is still not clear. It was suggested by McManus and Rempel[3] that the cross-linking in NBR solution hydrogenation might follow the von Braun mechanism (Figure 4-10). Von Braun[28] reported that nitrile group, hydrogen and catalyst are the factors triggering HNBR cross-linking, and the cross-linking is most likely caused by the side reaction that would be hydrogenation of the nitrile group. Once the nitrile group is hydrogenated, the viscosity of HNBR rises rapidly and continues to increase beyond 100% olefin hydrogenation. However, there is no nitrile hydrogenation in the experiments of this study because 1) no characteristic peaks of primary or secondary amines was observed at the range of 3200-3500 cm^{-1} in the FT-IR spectra of the hydrogenated NBR; 2) FT-IR peak of C≡N bonds (2236 cm^{-1}) remains unchanged throughout the reaction. As a result, the cross-linking in the present cases was not caused by the reaction of the nitrile group.

So far, there are no reports exploring the cross-linking in NBR latex system. Some reports have shown that $RhCl_3$ and selected ruthenium-phosphine (Ru-P) complexes catalyze the dimerization of acrylonitrile to adiponitrile in the presence of hydrogen[103,104]. Further studies revealed that the Rh- and Ru- trichloride are effective catalysts for the coupling of olefinic substrates in the absence of H_2 and the mechanism is quite similar to the Alderene reaction.[105] There could be such olefin-coupling side reactions in the hydrogenation of latex leading to the molecular weight increases.

Positional isomerization of olefins is another possible pathway initiated by $RhCl_3$ salts. Cramer *et al*. reported the migration of double bonds in different olefins under either a N_2 or H_2 atmosphere,[106,107]

and Jonassen reported an isomerization reaction in 1,5-cyclodecadiene.[108] In NBR, the distinctive IR stretch at 2,214 cm^{-1} of the conjugated olefin-nitrile system provides a means of monitoring positional isomerization development over the course of hydrogenation.

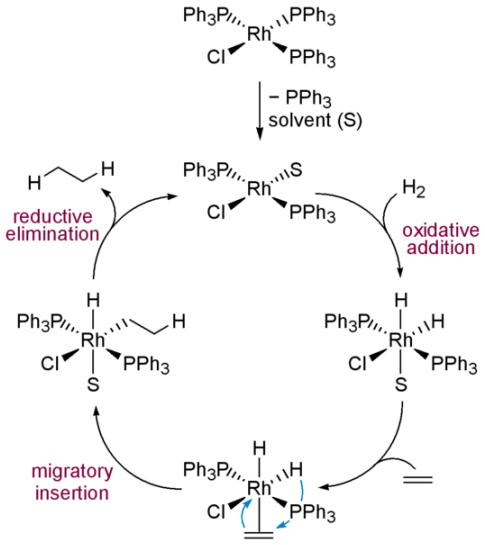


Figure 4-9 Catalytic cycle for hydrogenation with Wilkinson's catalyst[101,102]

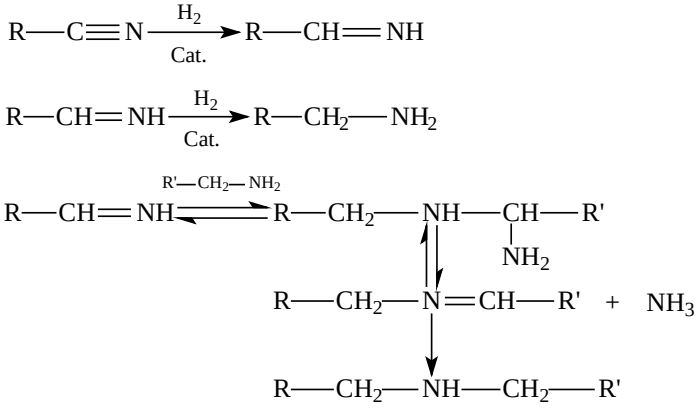


Figure 4-10 von Braun mechanism for nitrile hydrogenation in NBR hydrogenation[28]

As a result, a potential cross-linking mechanism is illustrated in Figure 4-11. By this reaction sequence, cross-linking results from a metal coupled NBR polymer to an activated olefin in another polymer. The activated olefin, by nature of its adjacent nitrile group, would be relatively electron deficient and therefore susceptible to reaction. Once it is reacted with the other polymer, the polymer

transforms from a 2D structure to a 3D network and cross-linking occurs. Therefore, this metal-mediated cross-linking process would be the combination of olefin migration and coupling.

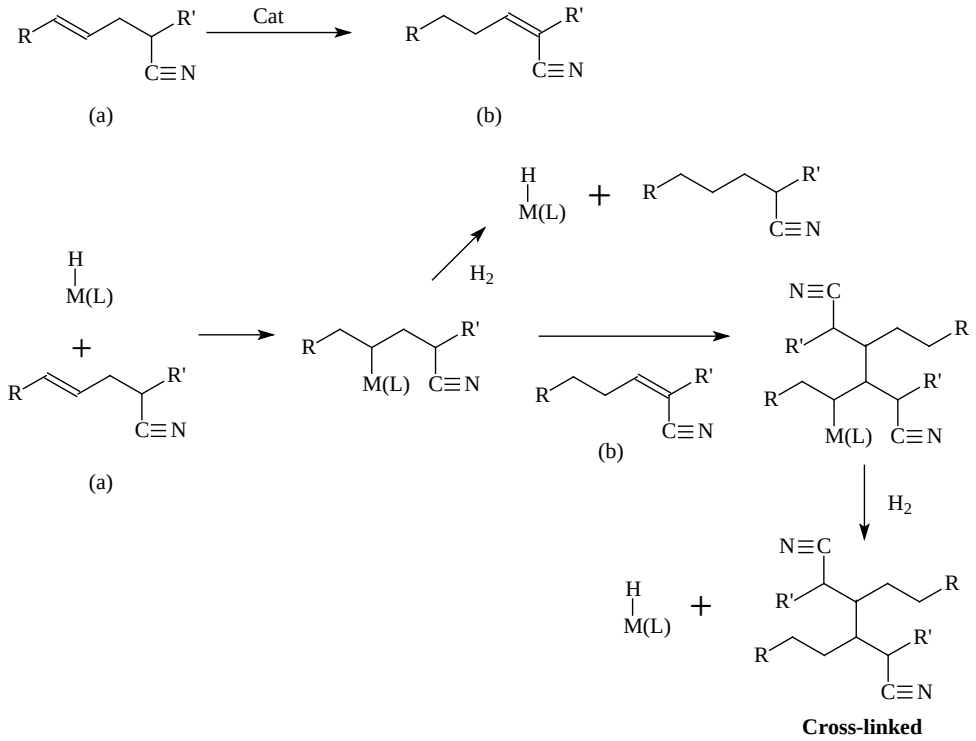


Figure 4-11 Potential olefin coupling mechanism

4.3.9 Characterization of NBR and HNBR in NBR Latex Hydrogenation

4.3.9.1 Comparison of Different NBR Latices

There are three types of latices that have been examined in the present work. They are all Perbunan brand made by Lanxess Inc., and have the same pH value and particle size, and similar polydispersity. Only Latex II has a little higher solid content, it is probably because Latex II was newly synthesized. Normally the solid content of the latex slightly drops as time goes on; the solid content of all the three was between 15–20 wt%. Latex I and III were used for NBR latex hydrogenation in most cases.

Table 4-2 Information of different NBR latices used in this work

Name		**Latex I** Perbunan latex F42-184/05	**Latex III** Perbunan latex T3429 2007-01	**Latex II** Perbunan latex T3429 2007-11
Receiving Date		**June 2005**	**Jan 2007**	**Nov 2007**
Color		**White**	**Light Pink**	**White**
pH value		**8**	**8**	**8-9**
Solid Content (wt%)	Self-measured	**15.67**	**17.06**	**19.42**
	Official	**15**	**17.14**	**19.5**
Particle Size	MN* (µm)	**0.0683**	**0.0679**	**0.0697**
	MA** (µm)	**0.0779**	**0.0772**	**0.0806**
	Standard Deviation	**0.021**	**0.02029**	**0.02119**
Polydispersity	Mw/Mn	**2.644±0.146**	**2.939±0.108**	**2.875±0.173**
	Mz/Mn	**10.747±0.911**	**8.652±0.430**	**11.931±1.345**
Molar Mass Moments (g/mol)	Mn	**8.010e+04 (5%)**	**1.921e+05 (3%)**	**8.079e+04 (5%)**
	Mw	**2.118e+05 (2.3%)**	**5.644e+05 (1.7%)**	**2.322e+05 (3%)**
	Mz	**8.609e+05 (6%)**	**1.662e+06 (3%)**	**9.639e+05 (10%)**

*: MN = Mean diameter, in microns, of the "number distribution" is calculated using the volume distribution data and is weighted to the smaller particles in the distribution. This type of average is related to population or counting of particles.
**: MA = Mean diameter of the "area distribution", which is calculated from volume distribution. It represents information on the distribution of surface area of the particles of the distribution.

4.3.9.2 FT-IR Analysis

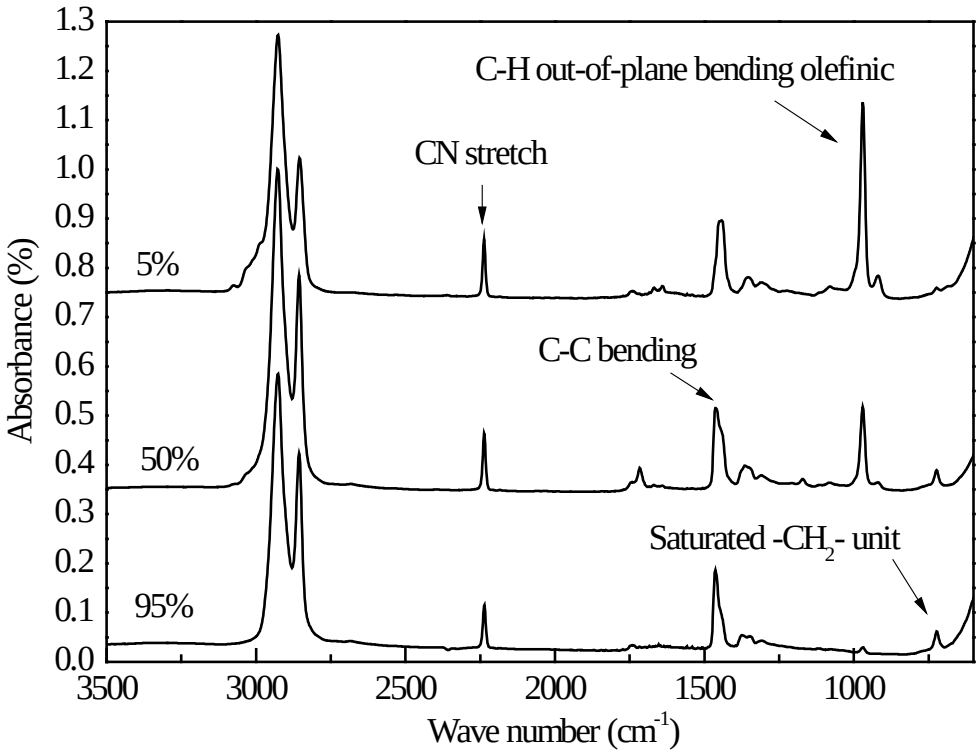


Figure 4-12 FT-IR spectra of NBR latex hydrogenation with different conversions

Perbunan latex F42-184/05 = 25 ml; water = 75 ml; catalyst/rubber = 0.5 wt%; TPP/rubber = 10 wt%; 600 rpm; 160^{o}C; H_2 = 1000 psig

Figure 4-12 depicts the FT-IR spectra of NBR latex hydrogenation using $RhCl_3$ with different conversions. The peaks at 2236 cm^{-1}, 970 cm^{-1}, 920 cm^{-1} and 723 cm^{-1} belong to -C≡N, =CH- in 1,4-trans unit, =CH- in 1,2 vinyl unit and saturated -$[CH_2]_n$- unit (n > 4) respectively. During the hydrogenation reaction, the intensity of peaks at 970 cm^{-1} and 920 cm^{-1} diminished considerably while the peak at 723 cm^{-1} appeared. The v(C≡N) was measured and it remained unchanged all the time, which indicates that Wilkinson's catalyst selectively hydrogenate C=C bonds and does not affect nitrile goups at all, so v(C≡N) was used as the internal standard for the calculation of conversion. There are no characteristic signals for primary or secondary amines in the spectra, confirming that the hydrogenation was completely selective towards the C=C bond in the latex system.

4.3.9.3 NMR Analysis

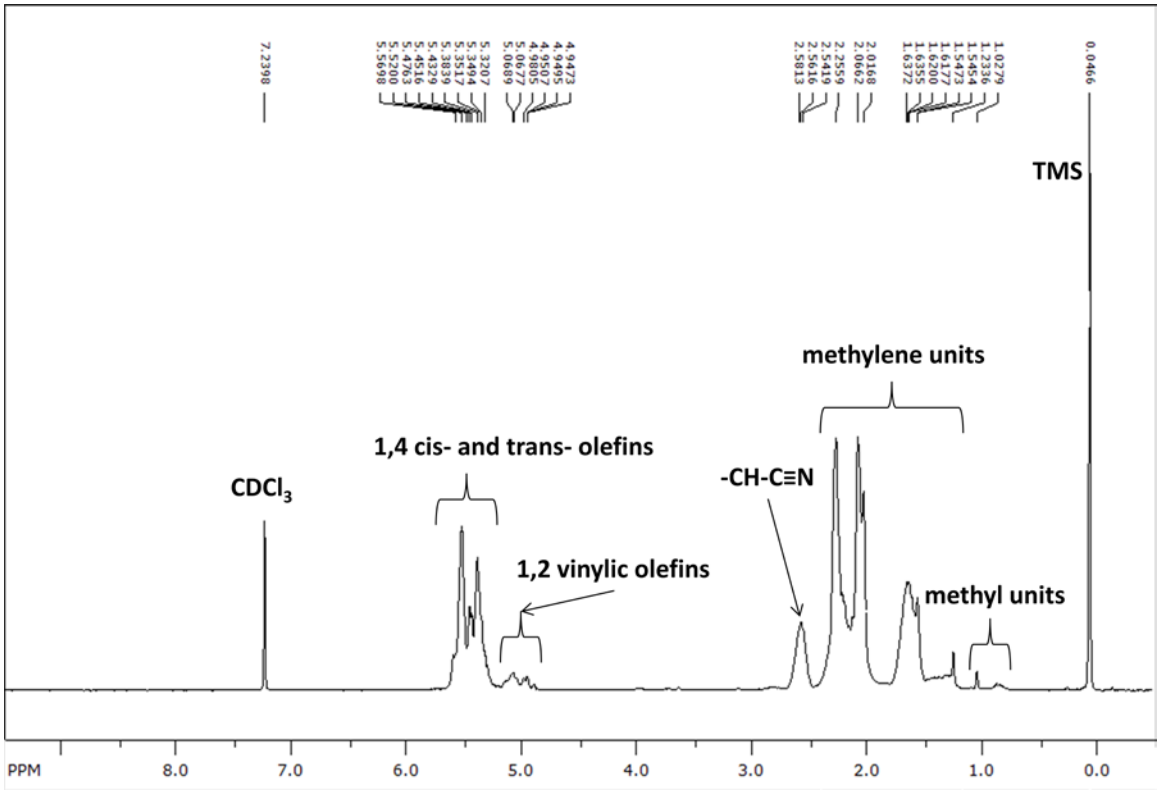


Figure 4-13 ^{1}H-NMR spectrum of NBR

Table 4-3 Peak assignments of ^{1}H-NMR spectra of NBR

Chemical shifts (ppm)	**Assignments**
0.05	Tetramethylsilane (TMS)
1.2-1.4	-CH_3 methyl units
1.6-1.7	-CH_2-CH< methylene units
2.0-2.1	-CH=CH-CH_2- methylene units
2.2-2.3	>CH-CH_2- methylene units
2.6	>CH-C≡N acrylonitrile units
4.9-5.1	-CH=CH_2- 1,2 vinylic units
5.3-5.6	-CH=CH- 1,4 cis- and trans- units
7.24	$CDCl_3$

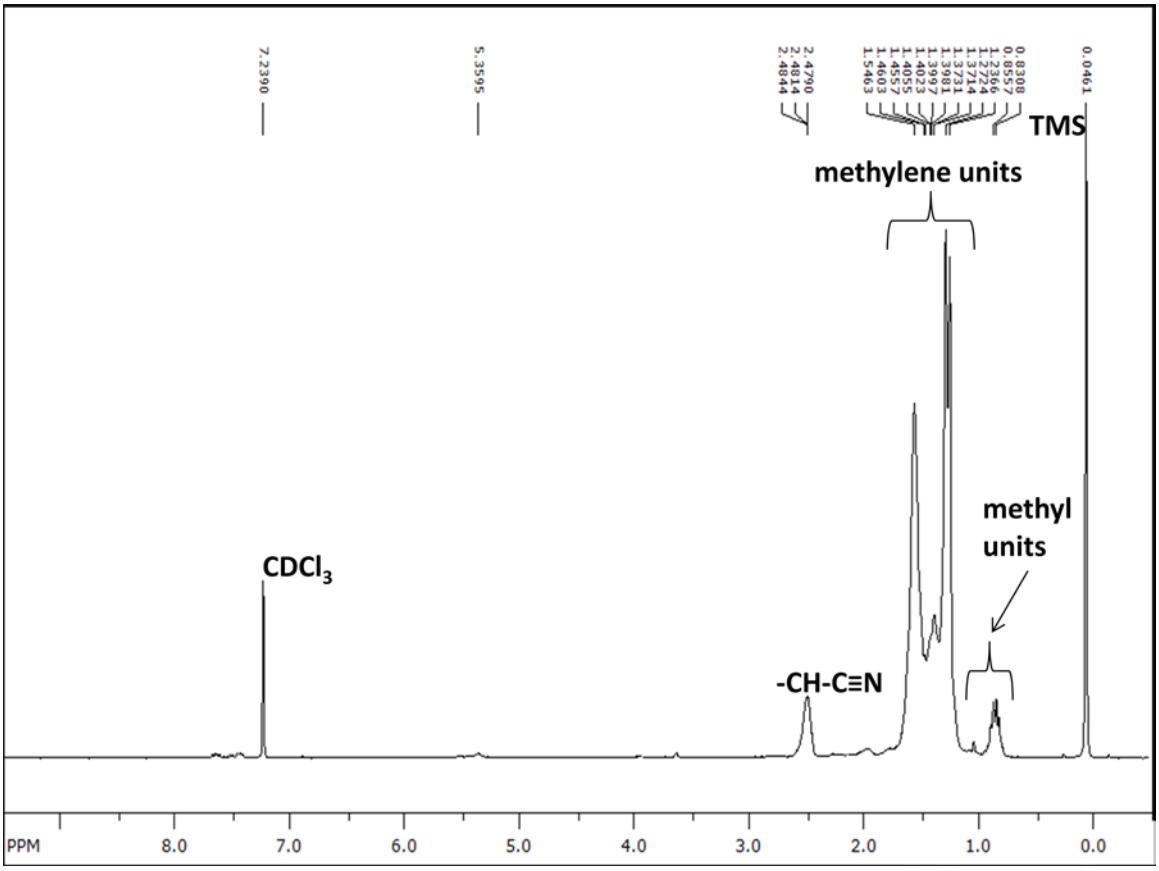


Figure 4-14 ^{1}H-NMR spectrum of HNBR (> 95%)

Table 4-4 Peak assignment of ^{1}H-NMR spectra of HNBR

Chemical shifts (ppm)	**Assignments**
0.05	Tetramethylsilane (TMS)
0.8-0.9	-C-CH_3- methyl units
1.2-1.4	-CH_2-CH< methylene units
1.5-1.6	-CH_2- methylene units
2.5	>CH-C≡N acrylonitrile units
5.3-5.4	-CH=CH- 1,4 cis and trans units
7.24	$CDCl_3$

Comparing Figure 4-13 and Figure 4-14 using the chloroform peak as a standard, the most significant difference is the absence or insignificant presence of -CH=CH- 1,4 cis and trans units, -CH=CH_2- 1,2-vinylic units, and -CH=CH-CH_2- methylene units in HNBR. This clearly implies that hydrogenation process has successfully taken place at the carbon-carbon double bonds in NBR converting them into saturated single bonds.

4.3.9.4 Particle Size, pH Value & Viscosity

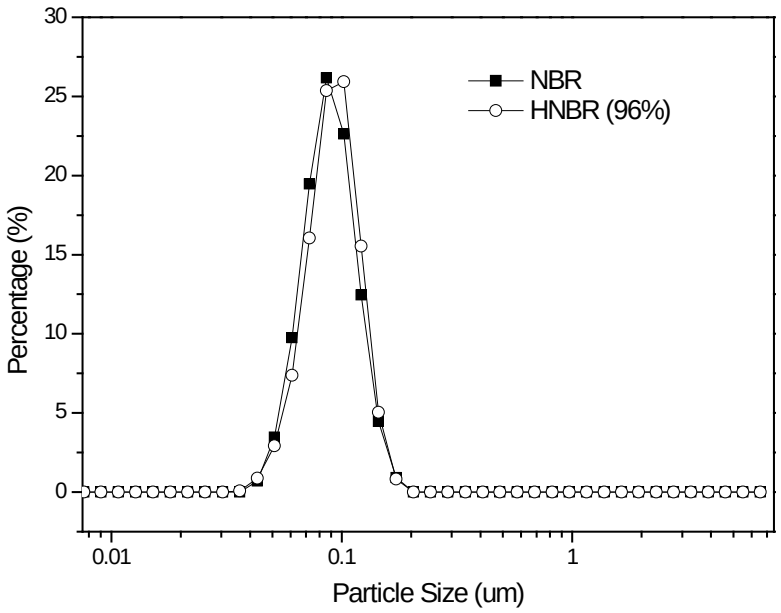


Figure 4-15 Particle size distributions in NBR latex and HNBR latex

During the hydrogenation process of the NBR latex, no coagulation was observed. The average particle size of the latex before and after hydrogenation remained almost unchanged (Figure 4-15), which means hydrogenation had no adverse effect on the latex particle size or stability.

To confirm the above conclusion, the viscosity of NBR latex and hydrogenated NBR latex was also measured using a Thermo HAAKE II rotational rheometer. Figure 4-16 shows the viscosity measured by a cone/plate unit; the viscosity slightly increases from 4 cP to 7 cP after hydrogenation of NBR latex which indicates the stability of latex does not undergo any large change. And the results from the cylinder unit (Figure 4-17) also show that the viscosity of hydrogenated NBR latex is around 6 cP which confirms the above conclusion.

The pH values of samples before and after hydrogenation were also monitored. The results show that the pH value of latex dropped from 8 to 6-7 after hydrogenation, which means that acid (HCl) was generated as suspected according to the synthesis of Wilkinson's catalyst. As discussed in previous sections, if the pH value can be kept constant, the gel formation may be well controlled.

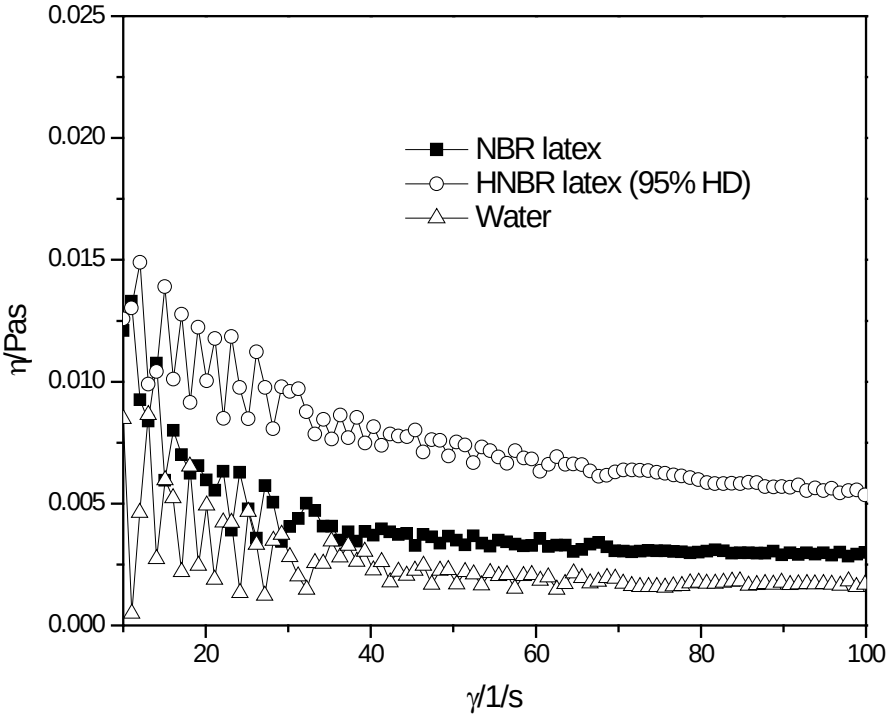


Figure 4-16 Viscosity of NBR latex, HNBR latex and water measured by cone/plate unit

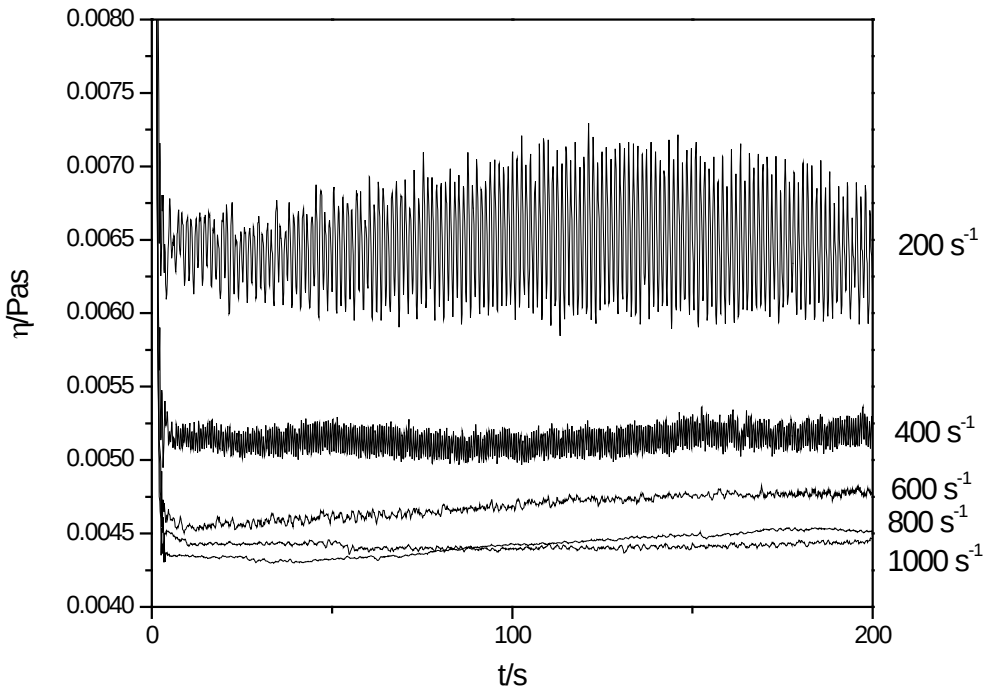


Figure 4-17 Effect of shear rate on the viscosity of HNBR latex (25°C) using Pz38b cylinder unit

4.4 Conclusions

NBR in the form of latex has been successfully hydrogenated to high conversion by using $RhCl_3$ without any organic solvent. NBR latex can be hydrogenated to a degree of more than 95% within 5 hours at 160°C using $RhCl_3$ in the presence of TPP with a catalyst/rubber ratio of 1.0% (w/w). The effect of TPP, reaction temperature, catalyst/rubber ratio, *in situ* synthesis of the catalytic active species and agitation speed were investigated.

Wilkinson's catalyst is synthesized *in situ* during hydrogenation. TPP is the co-catalyst ligand in the latex hydrogenation using $RhCl_3$. The catalyst for latex hydrogenation should be defined as $RhCl_3$/TPP. TPP is also a catalyst mass transfer promoter and reducing agent. Ethanol seems to be a very effective co-solvent for TPP and $RhCl_3$. Furthermore, the external or internal diffusion of H_2 should not be the rate limiting step for the overall hydrogenation process. The main concern for the whole process should be the catalyst mass transfer which includes:

a. Transport of the catalyst from the bulk water phase to the polymer particle surface area;

b. Intra-particle diffusion of the catalyst within the polymer particles;

Based on the current achievement, a successful $RhCl_3$/TPP catalyst system for NBR hydrogenation in the latex form has been initially developed which fulfills all major requirements (listed in section 3.1) for developing an organic solvent-free polymer latex hydrogenation route and is a significant milestone for the improvement of this polymer modification technology.

Chapter 5

Synthesis and Characterization of $RhH(P^iPr_3)_3$

5.1 Introduction

During the research on NBR latex hydrogenation, a search for new catalysts was carried out. Some catalysts were found and examined, and have shown very unique and promising characteristics. Based on our experience with olefin hydrogenation, a project was launched on hydrogenation of nitrile groups in HNBR and NBR, and considerable progress was achieved.

As stated in Chapter 2, most of the literature reports on nitrile hydrogenation (also called nitritle reduction or hydrogenation of nitriles) involve the hydrogenation of small-molecular nitriles, such as benzonitrile and valeronitrile. In the hydrogenation of nitriles, primary amines are not the only products; imines, secondary amines and sometimes tertiary amines are also formed from the reaction of imines and amines at the same time, as shown in Figure 5-1.

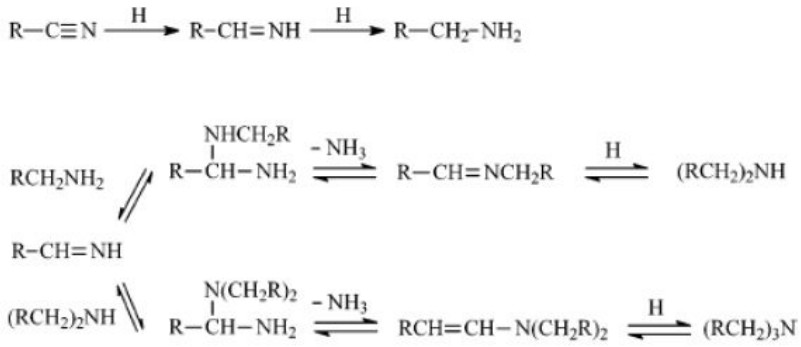


Figure 5-1 Formation of imine and amines in the hydrogenation of nitriles

Both homogeneous and heterogeneous catalysts have been investigated for the hydrogenation of nitriles, and hydrogenation with alternative hydrogen sources has also been reported. Homogeneous catalysts usually exhibit high selectivity for primary amines, and Rh, Ru and Ni catalysts have been widely investigated; however recovery of the catalyst is always a non-ignorable issue. On the other hand, heterogeneous catalysts, of which Pd and Ni catalysts are the most popular, have relatively poor selectivity to primary amines. As a result, some additives, such as NH_3 or some basic and acidic compounds have been used to improve their performance. Some unique techniques like biphasic and supercritical fluids have also been applied to achieve high selectivity and activity.[26,27,31,33-35,37-39,41-46,48-52,109]

Some of the reported methods for homo- and heterogeneous hydrogenation of nitriles are summarized in Table 5-1, for more details please refer to section 2.2. In the present case, the required hydrogenation degree of nitrile is not very high, so the catalyst activity should not be the main concern. Each NBR chain has on the average 500 nitrile groups; therefore trace amounts of secondary or tertiary amines generated in heterogeneous hydrogenation may cause serious gel formation of the rubber. Based on a summary from a literature review, it was decided to start with the homogeneous catalysts $RhH(PiPr_3)_3$ and $RuCl_2(PPh_3)_3$/t-BuOK.

Table 5-1 Summary of the catalysts used for hydrogenation of nitriles

Reduction System		**Remarks**
Heterogeneous Catalysts		> 99% selectivity with additives Removal of additives required
Homogeneous Catalysts	Rh	~100% selectivity, no need to remove additives
	Ru	> 99% selectivity with additionof base. Removal of additives required, gel formation
	Ni	Low selectivity, gel formation
Alternative H_2		< 96% selectivity. Removal of byproducts required

Our preliminary results indicated that the Ru catalyst system only works for benzonitrile whose C≡N group is attached to an aromatic group. Ru catalyst seems to be unable to reduce the C≡N group attached to a straight chain, which is also confirmed in the literature. Refer to Table 5-2 for details.

Table 5-2 Reduction of nitriles with Ru catalyst system[26,37-39,41-46,48-52,109]

Substances	**Results & Remarks**
NBR	No reduction of C≡Ns, C=Cs hydrogenated, gel formation
HNBR	
Acrylonitrile (Ch_2=CHC≡N)	No reduction of C≡Ns, C=Cs hydrogenated
Valeronitrile (C_4H_9C≡N)	No reduction of C≡Ns
Benzonitrile (C_6H_5C≡N)	C≡Ns reduced

For the Rh catalyst system, significant milestones have been achieved in the development of nitrile hydrogenation in macromolecules like polymers. A Rh hydrido complex, rhodium(I) hydrido tris(triisopropylphosphine) or tris(triisopropylphosphine)hydridorhodium(I), has been selected for nitrile hydrogenation and shown excellent performance. The catalyst's formula is $RhH(PPr^i_3)_3$, $RhH(P^iPr_3)_3$, $RhH(P(i\text{-}Pr)_3)_3$, or $RhH(PP^ir_3)_3$. With $RhH(PPr^i_3)_3$ the acrylonitrile percentage in NBR or HNBR can be controllably reduced from 40% to 10% or even lower in 5 hours under relatively

mild condition (hydrogen pressure and temperature etc.). This has never been achieved before this thesis. Moreover, tandem hydrogenation of nitrile and olefinic groups in NBR has been successfully carried out for the first time. In the following chapters, these results will be discussed in more detail.

5.2 Experimental

5.2.1 Materials

For the detailed information of the chemicals used in this chapter, please refer to section 3.2.1.

5.2.2 Equipment

The main equipment used in this work has been described previously, please refer to section 3.2.2.

5.2.3 Characterization

For FT-IR analysis, a certain amount of catalyst is fully dissolved in THF, then a small amount of catalyst solution is spread on a sodium chloride (NaCl) disk in a glove box (protected by argon gas) and allowed to dry. Once dry (a.k.a THF completely evaporated), the disk was placed in a gas-tight accessory (Demountable Pathlength Cell) which will be transferred out of the glove box and immediately tested in FT-IR with minimal air exposure. FT-IR was performed on a Nicolet 6700 FT-IR spectrometer. For the calculation of conversion of nitrile group, please refer to section 3.2.3.

For NMR analysis, $RhH(P(i\text{-}Pr)_3)_3$ was first dried and then made into several samples for subsequent examination. All samples were prepared in a glove box under an argon atmosphere. The samples were sonicated for at least 1 hour and left overnight, sealed with Parafilm in vials. The samples were sonicated for another 30 minutes or more the next morning, placed under an argon atmosphere in a glove box and then placed into clean NMR tubes. Caps were then sealed on with Parafilm to prevent air exposure when taken out of the argon environment for measurement.

5.2.4 Synthetic Procedure

This Rh hydrido complex has been brought to attention in 1960s and was later fully analyzed and characterized by Yoshida *et al.*[35,36] The following synthetic procedure being used in this study is based on the method described in the publication of Yoshida *et al.*[35] with further modifications.

Step I: A mixture of $RhCl_3 \cdot 3H_2O$ (0.98 g, 4 mmol) and P^iPr_3 (1.6 ml, 8 mmol) was stirred in 35 ml THF for 20 hours at room temperature. A brown solid residue was then obtained by concentration under vacuo.

Step II: THF (35 ml), P^iPr_3 (1.0 ml, 5 mmol) and 1% Na/Hg (40 g) were added sequentially to the brown solid. The mixture was stirred at room temperature for 20 hr. The filtered reaction solution was dried under high vacuum (0.001 mm Hg) to remove excess P^iPr_3.

Step III: Recrystallization of the resulting dark brown solid residue from pentane containing free P^iPr_3 (0.5 ml) gave $RhH(P^iPr_3)_3$ as yellow crystals (1.4 g, 60%). The reaction scheme of the catalyst synthesis is shown in Figure 5-2.

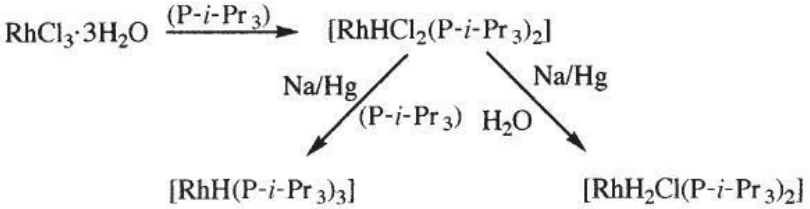


Figure 5-2 Synthesis of $RhH(P^iPr_3)_3$[110]

5.3 Results and Discussion

Many batches of the catalyst have been synthesized and an effort was made to improve the original synthetic techniques at the same time. The hydrous reagents were replaced by anhydrous ones. As shown in Figure 5-2, if water is present in Step II of the catalyst synthesis, side products might be produced which will result in no hydrogenation reactivity.

During the synthetic procedure, samples have to be dried in vacuum two times, one of which requires high vacuum of 0.001 mm Hg. The samples from Step I can be easily dried, however those from Step II sometimes encounter a little bit of difficulty in drying; some sticky liquid often remains at the bottom of vials. According to the literature,[36,111] one of the purposes of sample drying is to remove excess P^iPr_3 whose boiling point is 81°C at 22 mm Hg. The residue that cannot be dried may be excess P^iPr_3 or side-products which are believed to affect the following recrystallization. A new pump with better ultimate vacuum (0.0001 mm Hg) was purchased to address this issue.

In Step II, 1% sodium mercury amalgam is added to the solution to act as a reducing agent. Previously a batch of 1% sodium mercury amalgam was prepared at one time and stored it for future use. According to MSDS, when the concentration is 1% or less, Na/Hg is fluid; between 1% and 2.5%, it is doughy; with 2.5% and higher, it is a crystalline solid. The newly prepared 1% Na/Hg was fluid and not wall-sticking, however after a couple of weeks, it was found to undergo "dehydration" and became wall-sticky. In the experiments of this study, Na plays a very important role, so when Na/Hg was wall-sticky; it is very difficult to transfer an exact amount of amalgam into the solution, which of course lowered the yield of the desired catalyst.

The gas for degassing was changed from nitrogen to argon. As shown in Figure 5-3, the catalyst $RhH(P^iPr_3)_3$ could form $RhH_3(P^iPr_3)_2$ in the presence of H_2, however if there is any N_2 present it will continuously form a dinitrogen compound $RhH(N_2)(P^iPr_3)_2$, followed by other reactions if conditions permit. In the previous experiments, N_2 was used for degassing before introducing the catalyst solution into the system. While on the other hand, if $RhH(N_2)(P^iPr_3)_2$ does exist, there should be a peak for $-N_2$ at 1980 cm^{-1} in the FT-IR spectrum, however the results of the present work did not show any peaks in that area. Nevertheless, using argon was preferred.

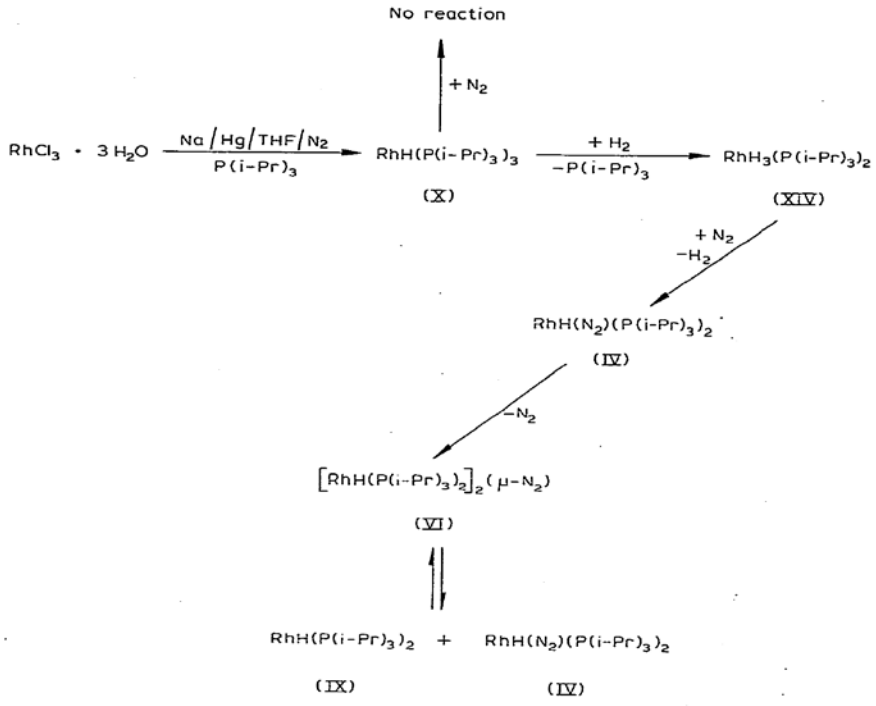


Figure 5-3 Scheme of preparation of different Rh hydrido compounds[35,112]

Overall, the above improvements made to the synthesis procedure improved the performance of the catalyst has been significantly improved (Figure 5-4). Previously it took about 20 hours to reduce the nitrile content from 40% to 5%; using the same amount of catalyst synthesized with improved procedure, the reaction time decreased to less than 5 hours. Many repeated synthesis were conducted, and the results are consistent and the error is within 5%.

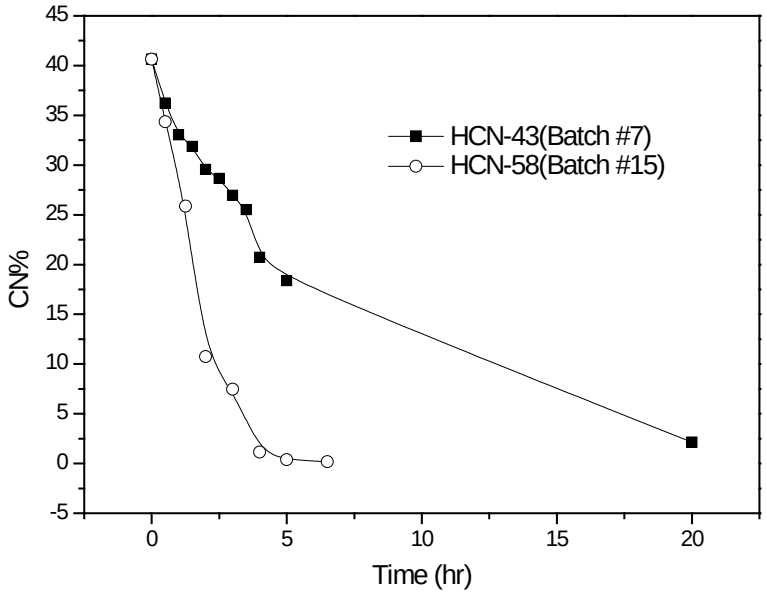


Figure 5-4 Improvement of catalyst performance after modification of synthesis procedure

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100 ml 2.5 wt% NBR in THF, 500 psig H_2, 60^{o}C

5.3.1 Experimental Challenges

The first challenge was the varying activities of the catalysts that were prepared. Typically, a new batch of catalyst was synthesized with each batch following an identical recipe**.** After each batch had been prepared, it was separated into two vials labelled A and B. This process was used without critical examination until it became clear that there was a significant variation in the behaviour not only of different catalyst batches, but between the divisions of the same batch as well. During this time, new iterations of the catalyst were prepared at a greater frequency, and the process with which they were synthesized was examined. It was discovered that the main cause of the variation in

catalytic activity was caused by the lack of complete dissolution of solids in the catalyst solution. The final product, tris(triisopropylphosphine)hydridorhodium(I), might contain some un-dissolved rhodium chloride powder (or other intermediates) which over time tends to form a thin layer of loose sediment inside the vial. This sedimentation explains how there is such an unusual disparity in catalyst efficiency between batches and within individual vials. This sedimentation issue is described pictorially in Figure 5-5.

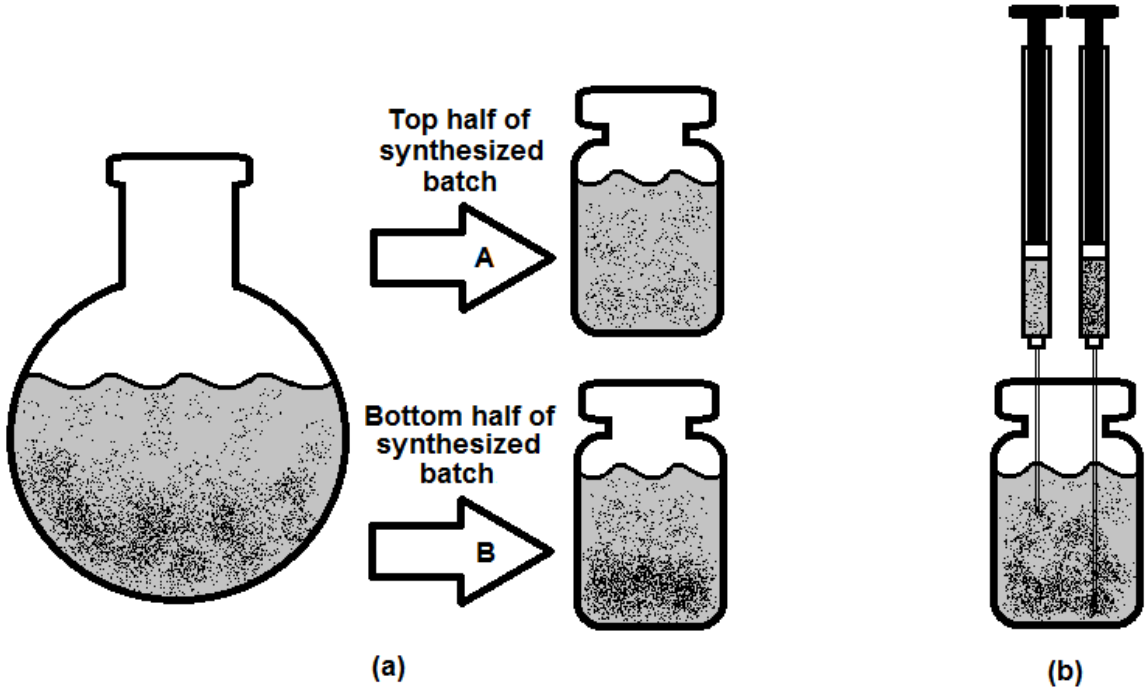


Figure 5-5 An illustration of the sedimentation of $RhCl_3$ powder within the catalyst solution

Image (a) illustrates how the division of the synthesized batch into two vials "A" and "B" can cause a discrepancy in catalyst potency. Image (b) illustrates the same principle within an individual vial, where a needle extracting the catalyst from the top of the vial has a less potent volume of the catalyst than the needle plunged further into the vial.

Before this problem was discovered, the vials were not thoroughly shaken to redistribute the rhodium chloride, so the catalyst at the bottom of the vial was significantly more potent than at the top. Similarly, it explains why the "B" catalysts were slightly more efficient than "A" catalysts of the same batch, since B catalysts contained the bottom half of the catalyst solution from the synthesis. Catalyst batches were then stored in single, large vials, and were shaken thoroughly before removal of

any catalyst solution, a process which has significantly improved the uniformity of the results, though different catalyst batches still experience minor differences in activity.

The second major challenge which occurred during experimentation was the formation of gel in the rubber solutions during hydrogenation. Gel formation is the result of cross-linkage of bonds forming inside the rubber solution, wherein long NBR or HNBR chains under specific conditions become bound to one another forming a polymer network which increases the viscosity of the rubber solution, changing it from a liquid into a mucus-like gel which flows much more slowly. In extreme cases, the rubber solutions gel completely wherein they conform and adhere to their container and have a gelatinous character. This was a minor challenge within the context of the experiment because it did not have any effect on the results; it only made collecting the samples more difficult due to the inability to pipette the samples and to cast a form onto NaCl disks. However, in a broader sense, gelling is a major challenge to polymer processing. Numerous experiments were performed in an attempt to isolate the factors which caused gel formation, though these experiments did not yield any conclusive results, and were in some cases apparently contradictory. In some cases, the solutions would be gelled inside the Parr reactor, whereas other solutions under identical conditions would remain liquid in the reactor, though gel rapidly when exposed to air. Currently there is still no clear understanding of the factors affecting gel formation, or the mechanism through which it occurs; more on this will be discussed in Chapters 6 and 7.

5.3.2 Characterization

5.3.2.1 FT-IR

FT-IR was performed using a Nicolet 6700 FT-IR spectrometer. After much research the peaks of the graph were labeled and are listed in the table below:

Table 5-3 Peak assignments of IR spectrum of $RhH(P(i\text{-}Pr)_3)_3$[113-121]

Bond or Bend	Wavenumber (cm^{-1})	Peak Height (Absorbance)
C-H Bond	2960, 2931, 2872	0.230, 0.037, 0.148
P-H Bond	2421, 2327	0.063, 0.040
C=O Bond	2350, 670	0.040, 0.030
Rh-H Bond	1984	0.010
O-H Bend	1664	0.051
C-H Bend	1458, 1385, 1367	0.017, 0.085, 0.049
P-H Bend	1177, 990	0.235, 0.074
C-H Bend (2)	900	0.234
P-C Bond	700, 687	0.093, 0.042

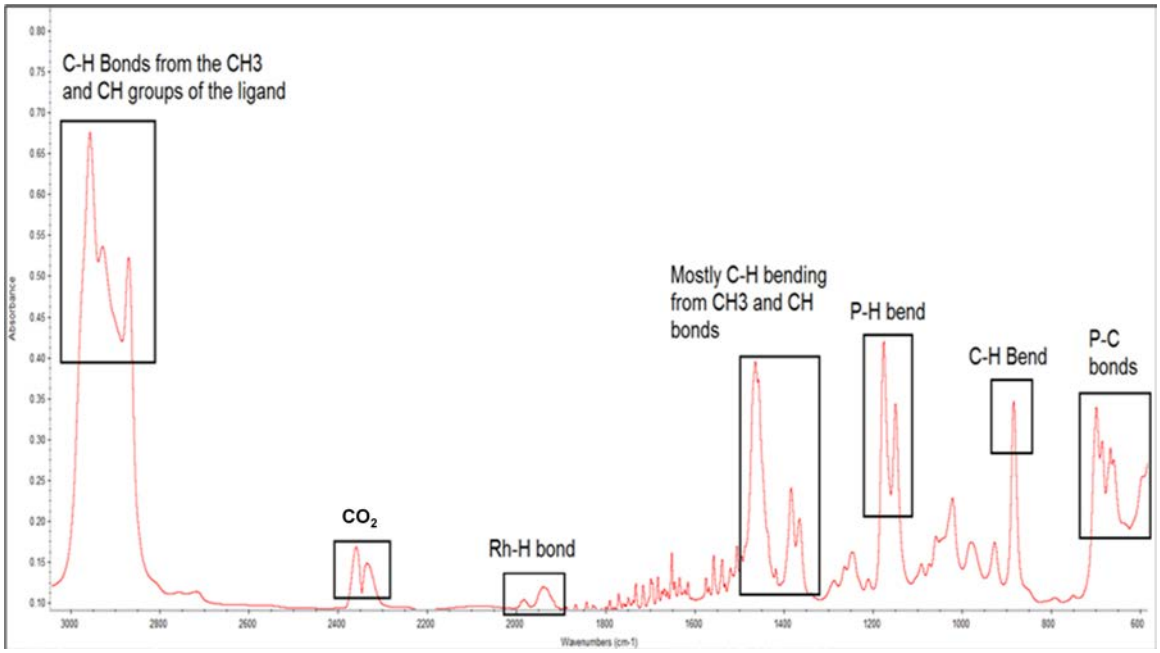


Figure 5-6 FT-IR spectrum of $RhH(P(i\text{-}Pr)_3)_3$

As we can see in Figure 5-6, there are very strongly defined peaks in the 2800 cm^{-1} to 3000 cm^{-1} region. These peaks are characteristic of the C-H bond in any alkanes, as the same as the ones in the Rh hydrido catalyst's ligand, $P(i\text{-}Pr)_3$. The small peak at 1980 cm^{-1} is the Rh-H bond. There are numerous papers to support this claim.[113-121] The peaks in the 1300-1500 cm^{-1} range are due to C-H bending. These signals are caused by the planar bending of the bond in 3-D space and are caused once again by the ligands attached to the catalyst. There is a noticeable P-H bend in the 1100 cm^{-1} to 1200 cm^{-1} range, a second C-H bending peak around 900 cm^{-1} and finally a couple of peaks in the 650-700 cm^{-1} range related to the P-C bond of the ligand.

5.3.2.2 NMR

5.3.2.3 The distinguished peaks in the NMR spectra are summarized below in

Table 5-4. The data are from several $^{31}P\{^{1}H\}$-NMR (proton decoupled) runs and thus displays any phosphorus environment. For the original NMR spectra please refer to Appendix B. The peak around 20 ppm is characteristic of the P-*i*Pr ligand of the catalyst[110,122]. The other peaks in the 50-70 ppm range may be attributed to the Rh-P bonds of the catalyst.[123,124] Though peaks of the current results are in the same region, they do not perfectly match those mentioned in other reports. There also seems to be some solvent effects as C_6D_6 appears different than the toluene-d_8, even if neither solvent has a phosphorus bond.

Table 5-4 $^{31}P\{^{1}H\}$-NMR data of $RhH(P(i\text{-}Pr)_3)_3$

Sample #	**Solvent**	**Peak (ppm)**					
0	Toluene-d_8	64.5922, s	63.2515, s	55.1200, h	54.4087,m	53.8272, h	20.7478, m
3	Toluene-d_8	70.1599, m	68.5080, m	57.1021, s	56.7935, h	56.1649, s	20.7469, m
1	C_6D_6			56.2176, h			
2	C_6D_6			56.7572, h			20.6708, m
Peak assignment		Rh-P bonds					P^iPr_3 bond

Note: s = small peak, m = medium peak, h = high peak.

5.4 Conclusions

The catalyst, tris(triisopropylphosphine)hydridorhodium(I), has been screened, selected and synthesized. This catalyst is used for the first time for the hydrogenation of nitrile and olefinic groups in HNBR and NBR in this study and has proven to be very effective. The synthetic procedure has been modified and the performance of the catalyst has been improved. Characterization of the catalyst was also carried out and is consistent with previous literature. More investigation of the performance of this catalyst will be shown and discussed in following chapters.

Chapter 6
Hydrogenation of Nitrile Groups in HNBR

6.1 Introduction

Over the past decades, a highly saturated nitrile group-containing copolymer rubber, as represented by hydrogenated acrylonitrile butadiene rubber (HNBR), has drawn considerable attention and has been playing an essential role in modern industry such as in the automotive engineering and oil exploration industry. The highly saturated nitrile group-containing copolymer rubber HNBR is superior in heat resistance, oil resistance, ozone resistance, etc., compared to common ones with plenty of carbon-carbon double bonds in the main chain structure such as acrylonitrile-butadiene rubber (NBR).[15] However, depending on the amount of nitrile group and content of unsaturated carbon-carbon bonds (double bonds), HNBR's cold resistance varies greatly compared to NBR. Generally, cold resistance can be enhanced by reducing a certain amount of the nitrile groups, but there is a big challenge as the cold resistance is not always improved by reducing the amount of nitrile group when increasing the degree of saturation. However, while vulcanizates obtained by vulcanizing this rubber can be improved for cold resistance, oil resistance, dynamic characteristics, etc., heat resistance and ozone resistance may be insufficient.[125]

Therefore, it is urgently required by many industries to improve cold resistance of highly-saturated nitrile group-containing copolymer rubber. To solve this problem, a lot of effort was made in the present study to find an effective catalyst, which has already been introduced in the previous chapter. This catalyst, for the first time, has been found to successfully hydrogenate nitrile groups in HNBR. Further investigation of this catalyst will be shown and discussed in this chapter.

6.2 Experimental

6.2.1 Materials

For the detailed information of the chemicals used in this chapter, please refer to section 3.2.1.

6.2.2 Equipment

The main equipment used in this work has been described previously, please refer to section 3.2.2.

6.2.3 Characterization

The conversion of carbon-carbon double bonds (hydrogenation degree) of HNBR was determined by FT-IR. In the FT-IR analysis, the sample solution was cast onto a sodium chloride crystal disk. The NaCl disk was dried and a polymer film formed on it before it was ready for FT-IR analysis. The degree of hydrogenation was calculated from the FT-IR spectra according to the peak strength. For the calculation of the conversion of nitrile group, please refer to section 3.2.3.

As listed in Chapter 3, the dynamic viscosity of the NBR solution and the hydrogenated product was examined using a Thermo HAAKE II rotational rheometer. To quickly evaluate the gel formation of hydrogenated product, filtration with a 0.45 μm syringe filter is used. The detailed method is as below. Attach the 0.45 μm syringe filter to a luer-lock syringe, fill the tube with 5-10 ml rubber solution and insert the plunger. Push the plunger and press the solution through the filter. If the solution passes the filter, it means there is no gel formation; if not or only very little passes through, it means gel is formed after hydrogenation.

6.2.4 Hydrogenation Procedure

Solutions of HNBR (2.5 wt%) in tetrahydrofuran (THF) were initially prepared and placed on a shaker for one day to allow for the complete dissolution of rubber.

The detailed information of experimental procedure has been described previously, please refer to section 3.2.4.

6.3 Results and Discussion

6.3.1 Effect of Experimental Conditions on Hydrogenation of Nitrile Groups in HNBR

6.3.1.1 Effect of Catalyst Loading

As already shown in Chapter 5, $RhH(PPr^{i}_{3})_3$ shows very good performance for hydrogenating nitrile goups in the HNBR system. Figure 6-1 shows the effect of different catalyst loadings. Adding 0.8 ml catalyst solution, the nitrile content was reduced to 17% within 5 hours. By increasing the catalyst from 0.8 ml to 1.8 ml, C≡N% was almost completely removed (reduced to 2%). However, continuing to increase catalyst amount to 1.8 ml or more does not seem to improve the rate of nitrile reduction. This is probably because the nitrile groups on the surface of HNBR particles have already been hydrogenated and the excessive Rh cannot get into the inner layers of the rubber particles. One thing

to note is that, when the catalyst amount is lower than 0.8 ml, almost no reaction was observed because gel formation dominates over the reduction of nitriles. The causes and mechanism of gel formation will be discussed in detail in section 6.3.3.

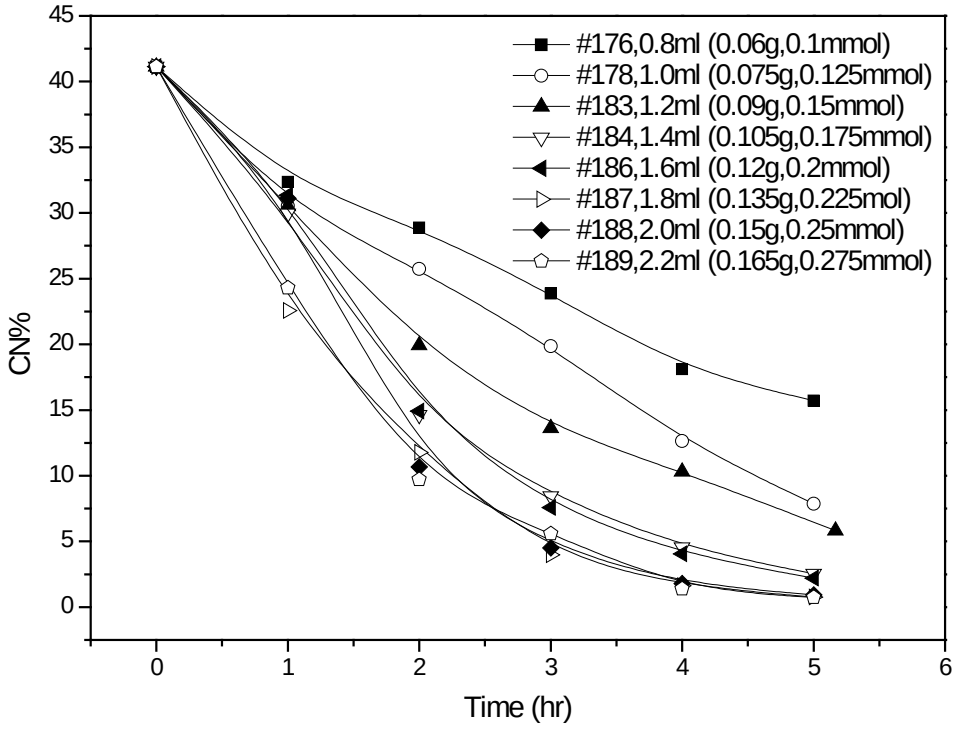


Figure 6-1 Effect of catalyst loading on hydrogenation of nitrile groups in HNBR

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100 ml 2.5 wt% HNBR in THF, 60^{o}C, 500 psig

6.3.1.2 Effect of Temperature

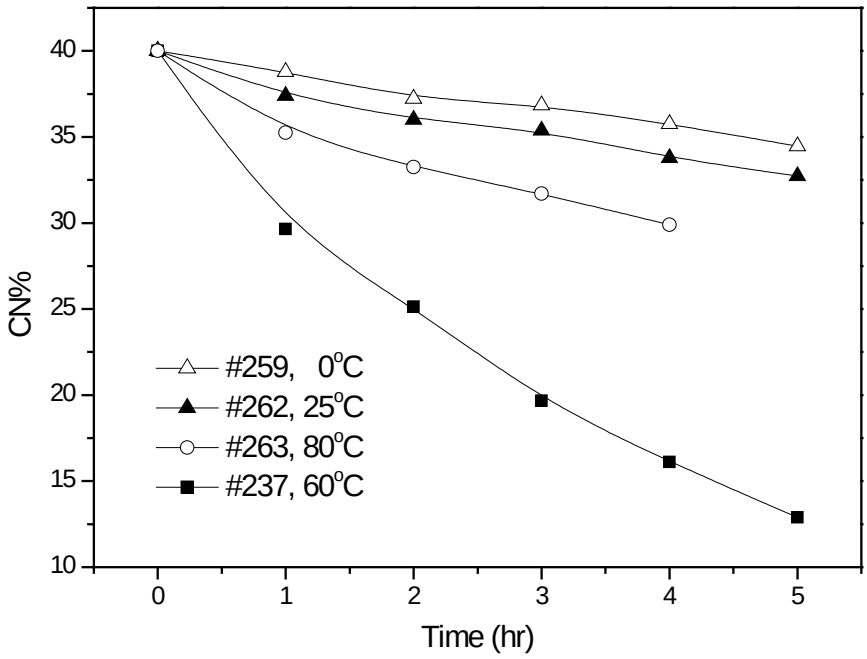


Figure 6-2 Effect of temperature on hydrogenation of C≡Ns in HNBR

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100 ml 2.5 wt% HNBR in THF, 500 psig

In addition to the effect of catalyst amount, the effect of different temperatures has also been investigated. A series of reactions were carried out at temperatures of 0°C, 25°C, 60°C, 80°C, 100°C, 120°C and 140°C. At 0°C, it takes 5 hours to reduce the nitrile percentage from 40% to 36%; while at room temperature C≡Ns can be reduced to 34% within the same period of time. On increasing the temperature to 60°C, the performance of the catalyst is immensely improved with only 12% nitrile groups remaining after 5 hours of reaction. It is obvious that high temperature induces faster movement of the molecules. However, when the temperature is 80°C or higher, although the reaction is much faster, gel formation occurs even faster such that; the rubber solution became complete gelled after just 1 hour, which made the measurement of sample very difficult and the actual measured values were very low (as shown in Figure 6-2). Consequently, 60°C seems to be the optimal reaction temperature.

6.3.1.3 Effect of H_2 Pressure

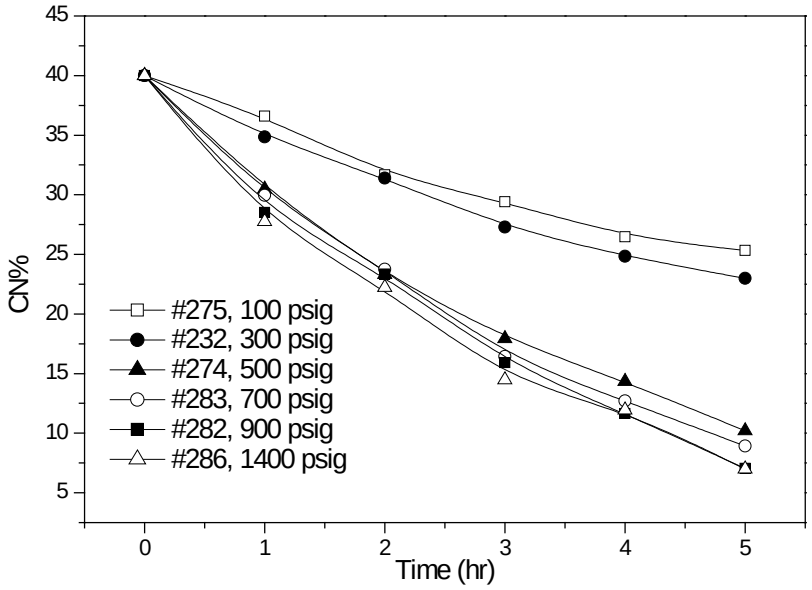


Figure 6-3 Effect of H_2 pressure on hydrogenation of C≡Ns in HNBR

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100 ml HNBR in THF (2.5 wt%), 60^{o}C

The effect of hydrogen pressure was also investigated and the results are shown in Figure 6-3. When the H_2 pressure is low (100 psig and 300 psig), there is not much difference for the rate of nitrile reduction; both curves end up at around 25% of nitrile content after 5 hours. However, reduction of nitrile becomes much faster when the hydrogen pressure equals 500 psig. The nitrile percentage drops to 10% within 5 hours. The possible reasons for this could be that the concentration of hydrogen becomes higher and more nitrile groups and hydrogen contact with the metal center of the catalyst. With the increase of pressure to 1400 psig, according to Figure 6-3, the reaction curves goes lower and lower; however the improvement is not as much as for the increase in pressure from 300 psig to 500 psig, which may be concluded that the hydrogenation rate is mainly controlled by the catalyst mass transfer within the rubber particles. The results clearly show that higher hydrogen pressure improves the catalyst's performance significantly. There might be two reasons for this; one is higher pressure increases the solubility of hydrogen in the solvent which is THF in current system; the other

is that, with the help of high hydrogen pressure, it is much easier for the catalyst molecules to transfer into the interior layers of rubber particles in order to hydrogenate more nitriles inside. For most of the experiments in this study, 500 psig is set to be the optimal reaction pressure.

6.3.1.4 Effect of Solvent

In most of the experiments in this thesis, THF was selected as the solvent, because THF is not only a good solvent for nitrile butadiene rubber, but for the catalyst being used as well. Other than THF, different solvents have also been investigated, such as MEK, acetone and MCB. However none of these were found to work for current system. In fact, the catalyst being used does have some activity in toluene; however toluene is not a good solvent for butadiene rubbers, so not much investigation has been carried out in toluene.

6.3.2 Preliminary Study of the Reaction Mechanism

After having conducted a large amount of experimental work, a possible reaction mechanism shown in Figure 6-4 is proposed for the first time in this study for the hydrogenation of nitrile groups in HNBR. Hydrogenation is performed under 500 psig hydrogen at a temperature of 60^{o}C using tris(triisopropylphosphine)hydrido-rhodium(I).

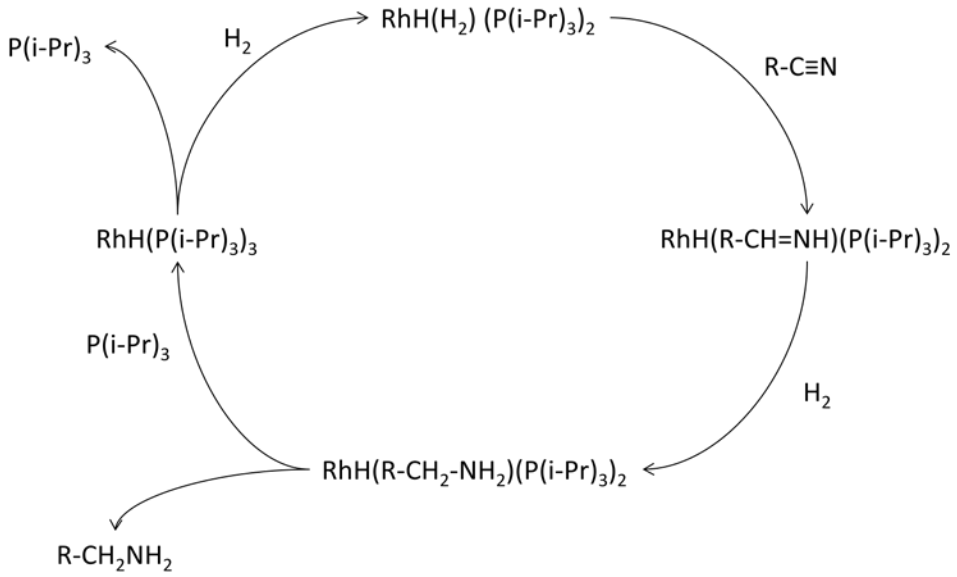


Figure 6-4 Proposed potential reaction mechanism for hydrogenation of nitrile groups in HNBR

The addition of hydrogen to the catalytic complex was reported by Yoshida, *et al.*[35,36] This addition creates a new five-member complex. A similar five-member complex with two chlorine atoms instead

of two hydrogen atoms has been reported by Butler *et al.*[110] This shows the complex proposed above is not unreasonable and a likely step in the catalysis of the hydrogenation reaction. The next step is a little more difficult to determine. A likely mechanism for this part of the reaction involves the rhodium complex reacting with the C≡N bonds along with hydrogen gas to reduce the nitrile to an amine. A more detailed and similar reaction is outlined in the Britannica Encyclopedia regarding catalytic hydrogenation of an olefin (alkene).[126] This reaction is shown below. "L" indicates a PPh_3 ligand. Similar additions to double and triple bonds were noted in a thesis paper by Lau,[127] further supporting the proposed reaction mechanism.

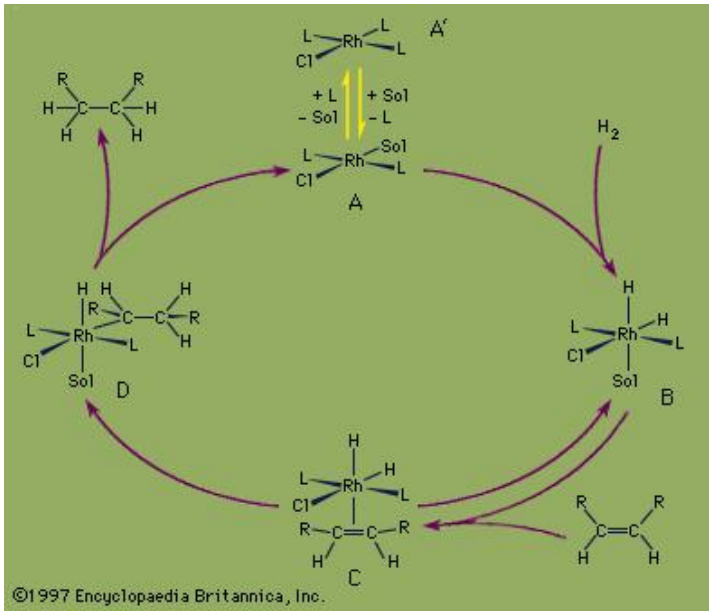


Figure 6-5 Mechanism for catalytic hydrogenation of alkene[126]

6.3.3 Gel Formation Reduction

So far, it has been so clearly shown that the nitrile groups in HNBR have been successfully hydrogenated and the whole process is clearly under control. However, the biggest issue throughout this study and also for rubber industry is gel formation. As discussed in previous chapters, the mechanism for gel formation (or severe cross-linking) is not clear and not fully understood. Based on experimental data of this study, some investigation on the causes and cure for gel formation were conducted, and some very promising results have been obtained, which will be discussed below.

6.3.3.1 Preliminary Study of the Causes for Gel Formation

Before finding a cure for gel formation, to find out the causes was believed to be crucial, so some investigation was carried out. An experimental system was set up involving the following factors: catalyst amount, hydrogen pressure, temperature, rubber concentration (NBR or HNBR), presence of air and all the factors were considered over a certain range using a method similar to an orthogonal experimental design. The reason that air is included in the investigation is to consider the case that degassing may not be adequate.

Table 6-1 Experimental factors for gel formation causes

Experimental Factor	Test Range
Catalyst concentration	1 mmol/L
H_2	15-500 psig
Air	15-100 psig
Temperature	25-100^{o}C
Rubber type	NBR, HNBR

After several series of experiments, it was observed that gel formation only occurs when rubber, hydrogen and catalyst are present at the same time; in other words, gel formed only when the reduction of the nitrile group occurs. It can be also concluded that if there is no reduction of the nitrile group, all the other factors, even air or high temperature could not initiate cross-linking. It is not by accident that another researcher's finding also confirms the conclusion of the present work. Zhou *et al*. stated, “the cause for the crosslink was investigated in three possibilities: (i) crosslinking caused by the hydrogenation of C≡N group; (ii) by the oxidation of C=C double bonds and (iii) by radicals in the system”.[25]

6.3.3.2 Further Study of the Causes for Gel Formation

As discussed in the above section, the factors of gel formation seem to be clear now. With the progress of the investigation in this work, something new has recently been discovered. First, many of the repeat experiments failed and the nitrile group could not be hydrogenated by the same catalyst at all; second, some NBR or HNBR solution became cross-linked by itself over a short period of time. Those phenomena captured our attention, and the reason was soon found that the THF being used was causing the problem. The THF of bad quality were not stabilized by a stabilizer. In industry, THF is often stabilized with 0.025% butylated hydroxytoluene (BHT) to inhibit the formation of explosive-prone peroxides which causes autoxidation (radical chain reactions that lead to decomposition).

Then a question comes to mind as to what would happen if there was no BHT present? The answer is clearly illustrated by Figure 6-6. Without BHT, THF easily reacts with air (oxygen in air) and produces a very active intermediate which soon forms two peroxides, 4-hydroxybutanoic acid lactone and 3-hydroxytetrahydrofuran, respectively. Those two peroxides are believed to be the causes for the failed experiments in this study. Besides having a negative effect on nitrile reduction in HNBR, it was also observed that THF peroxides inhibit hydrogenation of carbon-nitrogen triple bonds and carbon-carbon double bonds in NBR. More discussion on this topic is provided in Chapter 7.

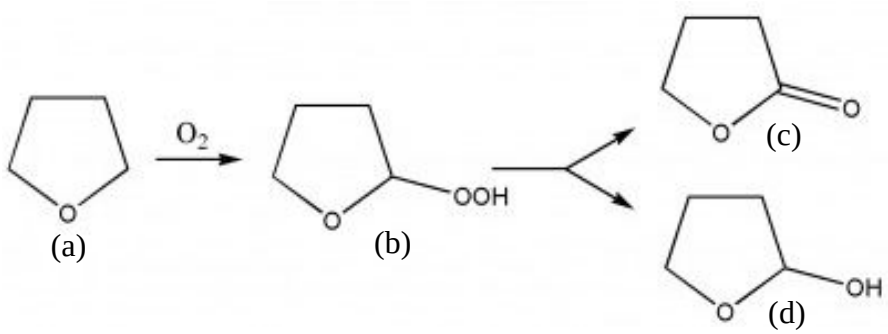


Figure 6-6 Oxidation of THF with air

(a) THF; (b) unstable intermediate; (c) 4-hydroxybutanoic acid lactone (γ-butyrolactone); (d) 3-hydroxytetrahydrofuran

As per the experiments carried out in this study, adding a small amount of BHT (< 250 ppm) does improve the performance of the catalyst to some extent and reduces gel formation to some extent. However, BHT is unable to reverse the autoxidation process. Consequently it is believed that the major factors influencing gel formation in nitrile reduction in HNBR are the nitrile goups, $-P(i\text{-}Pr)_3$ ligands of the catalyst and the THF peroxides, where the first two play more important roles.

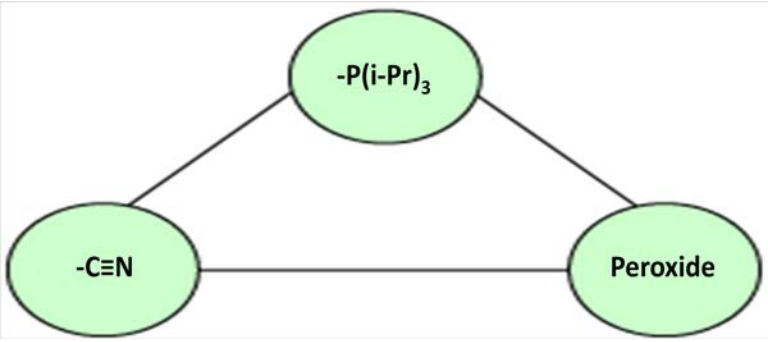


Figure 6-7 Major factors influencing gel formation

6.3.3.3 Effect of TPP on Gel Formation Reduction

The goal of this project is to reduce the percentage of nitrile in HNBR by 5% to 10%, and to prevent any formation of gel. As discussed so many times already, gel formation is one of the largest challenges. Fortunately, it was already found in this study that triphenylphosphine (TPP) is a very good additive for the NBR system (see Chapter 7 for detail). First, TPP terminates the hydrogenation of nitrile, and it does not affect the hydrogenation of the remaining carbon-carbon double bonds; the second and most important point is that no visible gel was observed when adding TPP for cases of low nitrile reduction.

With the successful findings for the NBR system, TPP logically became the first option for utilization in the HNBR system. To minimize the gel formation to as slow as possible while maintaining a relatively fast reaction, all experiments have been carried out at room temperature (25^{o}C). To make sure that only 5-10% nitrile reduced, TPP was added at about 50-60 min after addition of the catalyst (initiation of the reaction). Initially, a small amount of TPP was added, and no promising results were obtained. After increasing the amount of TPP, some very promising results were obtained which are shown in Table 6-2. These results clearly show that the complete gelling time has been significantly extended from overnight to about 2 weeks by adding 5-7.5 g TPP. Figure 6-8 confirms that the viscosity of the samples with addition of TPP was much lower than the regular ones. Amounts of TPP of more than 7.5 g were also tested, however no further improvement was observed.

Table 6-2 Effect of TPP on reducing gel formation in HNBR*

Experiment #	Catalyst	TPP** Used (g)	Time after addition of TPP (hr)	Time before complete gelling (day)
K41	#35	5	4	7
K38	#34	7.5	4	10
K47	#35	7.5	2	14
K43	#34	7.5	1	14

*: 0.8 ml catalyst solution (0.06 g, 0.1 mmol Rh), 100 ml 2.5 wt% HNBR in THF, 25^{o}C, 500 psig H_2
**: TPP was added after 50-60 min of addition of catalyst

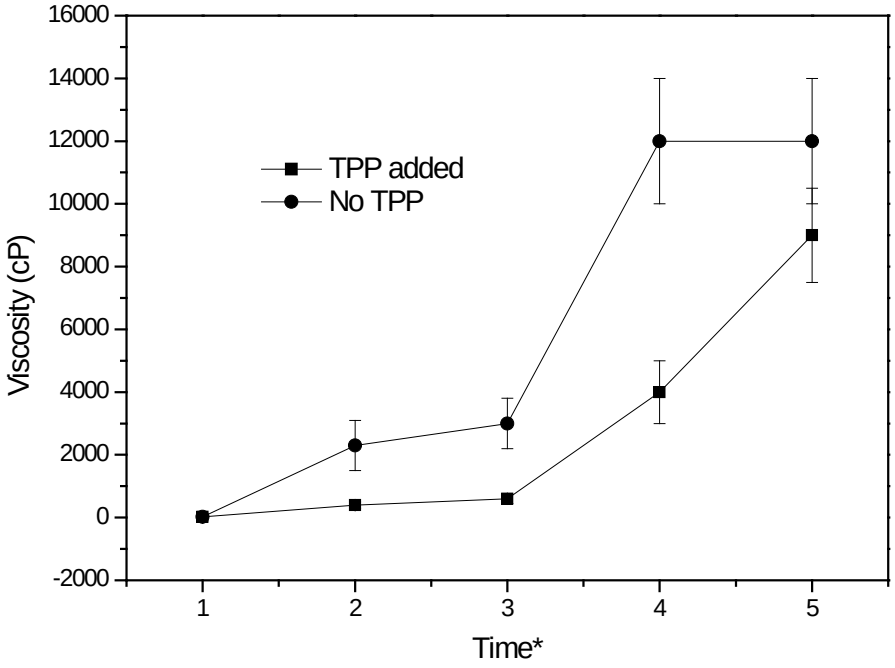


Figure 6-8 Viscosity change of nitrile-reduced HNBR with and without TPP as an additive*

*: 1 = before hydrogenation; 2 = 5 hr; 3 = 1 day; 4 = 7 days; 5 = 14 days

Regarding the function of TPP, the following dynamic equilibrium has been proposed and is quite likely,

$$RhH(P^iPr_3)_3 + PPh_3 \longleftrightarrow RhH(PPh_3)_4 + P^iPr^3$$

As shown above, when TPP is added, TPP ligands start replacing P^iPr_3 ligands of the initial Rh hydrido complex until an equilibrium that lies far to the right is reached which takes at least 1 hour. Since the original catalyst disappears, no more nitriles would be reduced, and consequently no gelling occurs. To avoid any contact with air or oxygen, the product was stored in a glove box filled with argon gas. More discussion will be provided in section 7.3.3.

6.3.3.4 Effect of TNPP

Other than TPP, other alternative additives have been examined for reduction of gel formation. Phenolic antioxidants have long been known for their protective properties against oxidation. It was

also found that tris(nonylphenyl) phosphite (TNPP) was an effective additive. Due to its structure (Figure 6-9) and property, TNPP normally works as an antioxidant and it is able to donate hydrogen to alkyl radicals that are present in the rubber during the hydrogenation process. With fewer radicals present, gel formation can be greatly suppressed, and the results are shown in Table 6-3. Without using any additives, the nitrile-reduced HNBR will start gelling after 2 hours and becoming completely gelled when left overnight. Adding a certain amount of TNPP does extend the period before gelling. With 10 g TNPP, the time before gelling is more than 2 days (50 hours). Although it seems that the gel-reducing performance of TNPP is not as good as TPP, the samples with TNPP (taken out of the reactor right after the reaction) can pass through a 0.45 μm filter without any problem whereas samples from the TPP addition reaction are slow to pass through the filter.

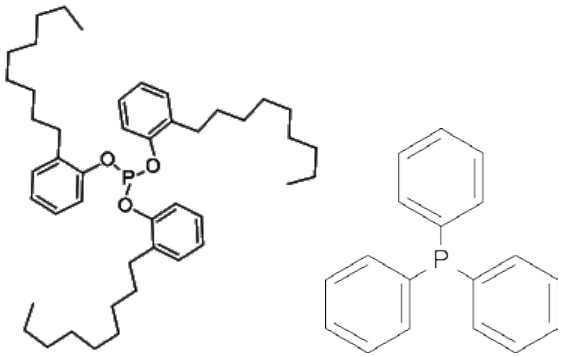


Figure 6-9 Structure of TNPP (left) and TPP

Table 6-3 Effect of TNPP on reducing gel formation in HNBR*

Experiment #	Catalyst	T (°C)	TNPP (g)	Addition Time of TNPP	Time Before Gelling
K48	#36	22	0	N/A	2 h
K19	#33	60	0.3	1 h	1 h
K20	#33	22	1	2 h	3 h
K21	#33	22	5	45 min	1 d
K28	#34	22	7.5	50 min	1.5 d
K26	#33	22	10	50 min	2 d
K27	#33	22	10	50 min	2 d

*: 0.8 ml catalyst solution (0.06 g, 0.1 mmol Rh), 100 ml 2.5 wt% HNBR in THF, 25^{o}C, 500 psig H_2

6.3.3.5 Effect of THF Peroxides

According to section 6.3.3.2, oxidation of THF with air produces some peroxides, which are 4-hydroxybutanoic acid lactone or gamma-butyrolactone (γ-BLT) and 3-hydroxytetrahydrofuran (3-HTHF). They not only inhibit the hydrogenation of the nitriles in HNBR, but also cause gel formation. As a result, very small amount of these peroxides was added to terminate the reaction and avoid unwanted gelling. Table 6-4 shows the results that even a very small amount of these THF peroxides causes very severe cross-linking, although they do terminate the hydrogenation process efficiently.

Table 6-4 Effect of THF peroxides on gel formation in HNBR*

Experiment #	Catalyst	Additive	
		3-HTHF (ml)	γ-BLT (ml)
K1	#32	0	/
K2	#32	0.1	/
K3	#32	0.5	/
K4	#32	0.5	/
K5	#32	/	0.5
K7	#29	/	0.8
K6	#29	/	1
K8	#29	/	2

*: 0.8 ml catalyst solution (0.06 g, 0.1 mmol Rh), 100 ml 2.5 wt% HNBR in THF, 25^{o}C, 500 psig H_2

6.3.3.6 Effect of Amines

Based on previous findings and accomplishments of our group, amines have previously been found to play a very important role in the hydrogenation process preventing or reducing cross-linking. N, N-diphenyl-p-phenylenediamine and N-phenyl-2-naphthylamine were examined; unfortunately they do not seem to be effective for the reduction of gel formation.

6.3.4 Characterization

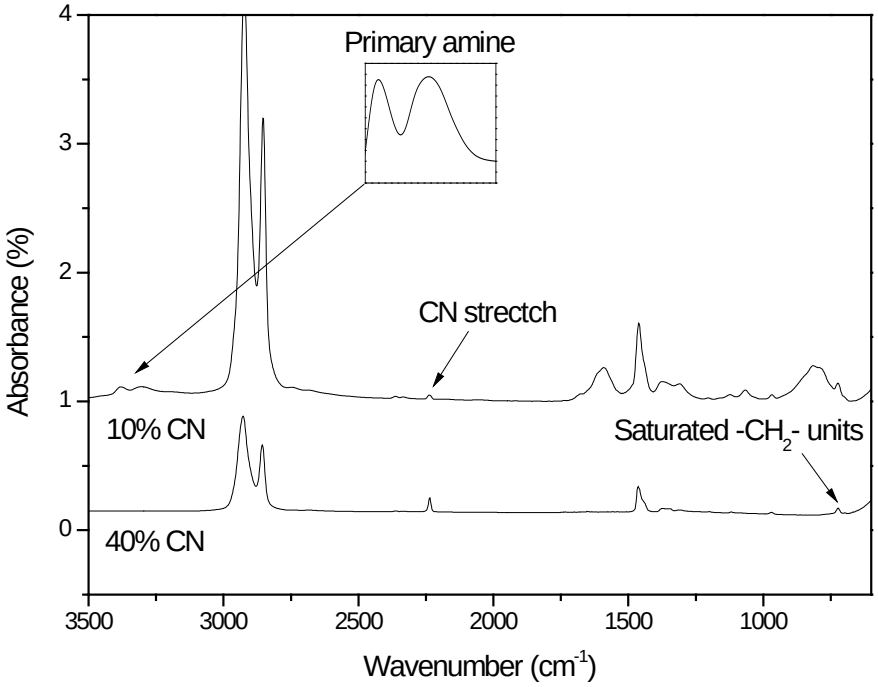


Figure 6-10 FT-IR spectra of HNBR with different acrylonitrile content

Figure 6-10 depicts the FT-IR spectra of hydrogenation of nitrile groups in HNBR with different conversions. The peaks at 2236 cm^{-1} and 723 cm^{-1} belong to -C≡N and saturated -$[CH_2]_n$- unit (n > 4) respectively. Since this is HNBR, there are no peaks for unsaturated carbon-carbon bonds at the 920-1000 cm^{-1} region. During the hydrogenation reaction, the v(C≡N) decreases and two bumps at 3200-3400 cm^{-1} appear which are the classic peaks of primary amines. No secondary amines or other types of amines (widely reported side products) are observed. The 723 cm^{-1} peak does not change and the nitrile peak (2236 cm^{-1}) almost disappears when nitrile content is about 10%, which means the catalyst is selectively effective for the hydrogenation of nitrile. The new peak of primary amines confirms that nitrile groups have been successfully converted to amine groups without any side products.

6.4 Conclusions

It has been shown that $RhH(PPr^{i}_{3})_3$ is capable of hydrogenating the nitrile groups in HNBR. The nitrile content can be reduced from 40% to less than 10% within 5 hours at 60^{o}C and 500 psig H_2. The nitrile groups have been converted to primary amines. A potential mechanism for nitrile hydrogenation has been proposed for the first time. Gel formation issues exist during a regular procedure, and temperature and catalyst concentration seem to aggravate gel formation. The causes for gel formation during nitrile reduction have been investigated and a possible mechanism was proposed. Some additives have been tested and some of them are found to be effective to slow down or terminate gel formation. TPP is the most effective additive. At last, it is worthwhile to point out that for the first time a successful system has been developed and established for the reduction of the nitrile content of HNBR (macromolecules) without visible gel formation

Chapter 7

Tandem Hydrogenation of Nitrile and Olefinic Groups in NBR

7.1 Introduction

Acrylonitrile butadiene rubber (NBR) is a very versatile rubber and is used extensively in the automotive and other industries. It is highly coveted in these industries due to its ability of being oil, fuel and chemical resistant. NBR is defined by its acrylonitrile (ACN) content which can have a drastic effect on the properties of the rubber. Changes in ACN content can change the properties of NBR due to the polarity of the nitrile bond. Increased polarity due to the presence of more nitrile bonds will have an effect on the rubber's ability to interact with other polar or nonpolar polymers. NBR with higher ACN content will have improved processability, oil/fuel resistance, air/gas permeability, tensile strength and abrasion resistance, while NBR with lower ACN content will have improved compression set, resilience, hysteresis and low temperature flexibility.[128]

As already shown in Chapter 6, an effective catalyst, $RhH(PPr^{i}_{3})_{3}$, has been screened, selected and proven to successfully hydrogenate the nitrile groups in HNBR. With addition of some amount of TPP or other additives, gel formation has been significantly reduced and controlled. However, if the same catalyst can be used in NBR system, which means to hydrogenate the nitrile groups and olefinic groups at the same time, it would be of great benefit for industries, such as saving cost and time etc. In this chapter, the investigation of hydrogenation of nitrile and olefinic groups in NBR will be discussed.

7.2 Experimental

7.2.1 Materials

For the detailed information of the chemicals used in this chapter, please refer to section 3.2.1.

7.2.2 Equipment

The main equipment used in this work has been described previously, please refer to section 3.2.2.

7.2.3 Characterization

Please refer to section 6.2.3 and section 3.2.3.

7.2.4 Hydrogenation Procedure

Solutions of NBR (2.5 wt%) in tetrahydrofuran (THF) were initially prepared and placed on a shaker for one day to allow for the complete dissolution of the rubber.

The detailed information of experimental procedure has been described previously, please refer to section 3.2.4.

7.3 Results and Discussion

7.3.1 Effect of Different Experimental Conditions

7.3.1.1 Effect of Catalyst Loading

In Figure 7-1, it is clearly shown that the reaction rate of hydrogenation becomes faster and faster upon increasing the amount of catalyst added, which is similar to the cases of NBR latex and HNBR (Chapters 4 and 6, respectively) and is also very reasonable for a homogeneous catalytic system. When 1.2 ml (0.12 g) catalyst was added, the percentage of C≡N can be reduced from 40% to almost 0% within 4 hours. However, the accompanying problem is that gel formation becomes more severe with increased amount of added catalyst. Amounts of catalyst over 1.2 ml have been carried out as well, but the rapid gel formation made the samples impossible to be taken and evaluated. As discussed in Chapter 6, there might be two causes for this; one is the catalyst itself, due to its large amount, which causes gel formation; and the other being the breaking of carbon-nitrogen triple bonds, in such a short time, which may generate many radicals which causes severe cross-linking.[129] Also, since this is an NBR system, there are many carbon-carbon double bonds available, and the catalyst

actually is doing two jobs; one is hydrogenating unsaturated C=C bonds and the other is hydrogenating C≡N triple bonds. As a result, breaking of both C=Cs and C≡Ns might make chain tangling more easily and cause more severe cross-linking. Tandem hydrogenation of olefinic groups and nitrile groups will be discussed in later sections in this chapter.

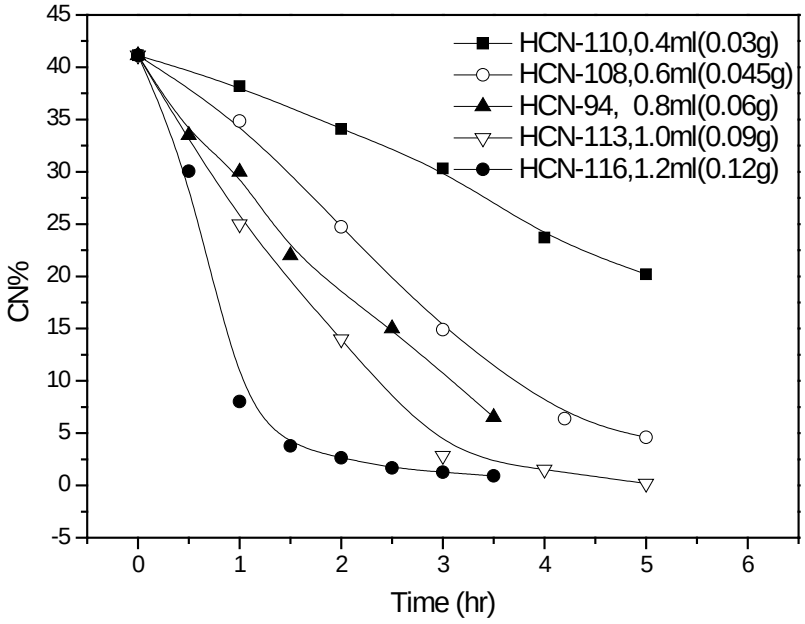


Figure 7-1 Effect of catalyst loading on hydrogenation of C≡Ns in NBR

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100 ml 2.5 wt% NBR in THF, 60^{o}C, 500 psig

7.3.1.2 Effect of Temperature

The effect of the reaction temperature has been investigated as usual. With increasing temperature from 5^{o}C to 100^{o}C, the activity of catalyst was greatly improved due to faster movement of molecules of both catalyst and rubber. More related discussion can also be found in section 4.3.2 and section 6.3.1.2. At 5^{o}C, C≡N% decreased from 40% to 35% within 8 hours, while at 100^{o}C, C≡N% decreases to 20% after 2 hours. In both cases, visible gel formation was observed. For temperatures greater than 100^{o}C, it was found that gel forms so fast that samples could hardly be taken out or evaluated by FT-IR. Factors for gel formation will be discussed in a following section.

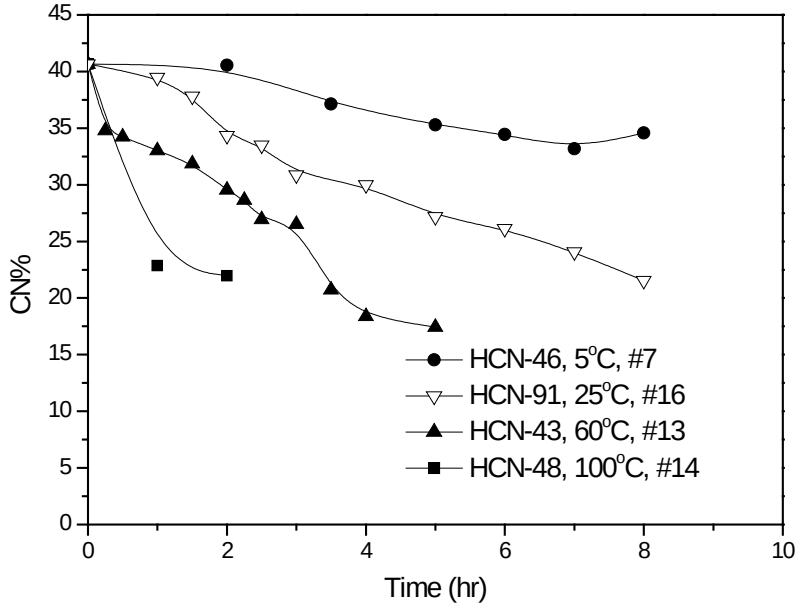


Figure 7-2 Effect of temperature on hydrogenation of C≡Ns in NBR

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100 ml 2.5 wt% NBR in THF, 500 psig

7.3.1.3 Effect of H_2 Pressure

Similar to the effect of catalyst loading, by increasing the hydrogen pressure from 100 psig to 500 psig, the performance of the catalyst can be improved significantly due to higher concentration of hydrogen and more chances for olefinic and nitrile groups to react with the metal center of the catalyst. When the pressure is increased from 500 psig to 900 psig, the acrylonitrile content does not decrease too much. It may be concluded that the hydrogenation rate is mainly controlled by the catalyst mass transfer within the NBR particles, which complies with the conclusions about NBR latex and HNBR discussed in previous chapters. At 100, 300, 500, 700 and 900 psig, the residual C≡N% after 5 hours is 30%, 15%, 8%, 5% and 4%, respectively. The results are shown in Figure 7-3. When H_2 pressure is 1000 psig or higher, both reduction of nitrile groups and gel formation was very fast, and severe visible gel was observed after just 1 hour.

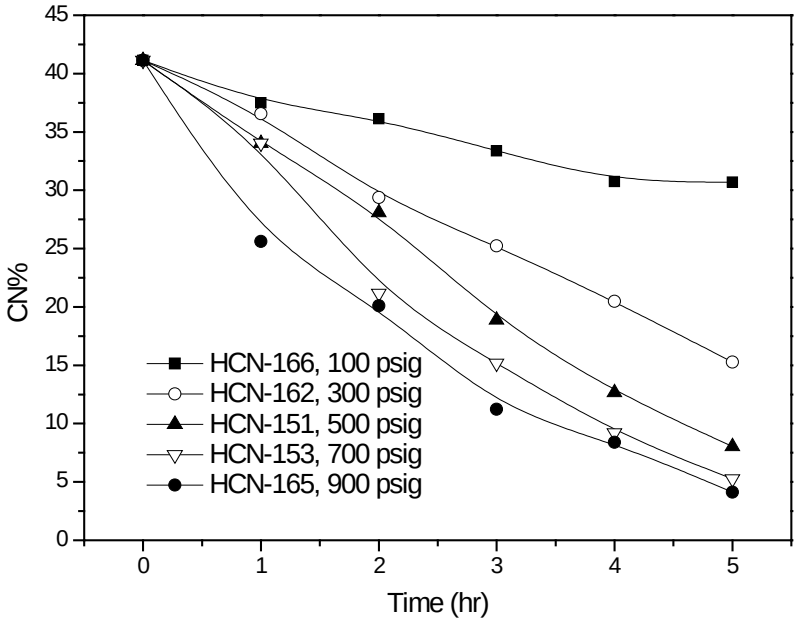


Figure 7-3 Effect of hydrogen pressure on hydrogenation of C≡Ns in NBR

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100 ml 2.5 wt% NBR in THF, 60^{o}C

7.3.1.4 Effect of Concentration of NBR Solution

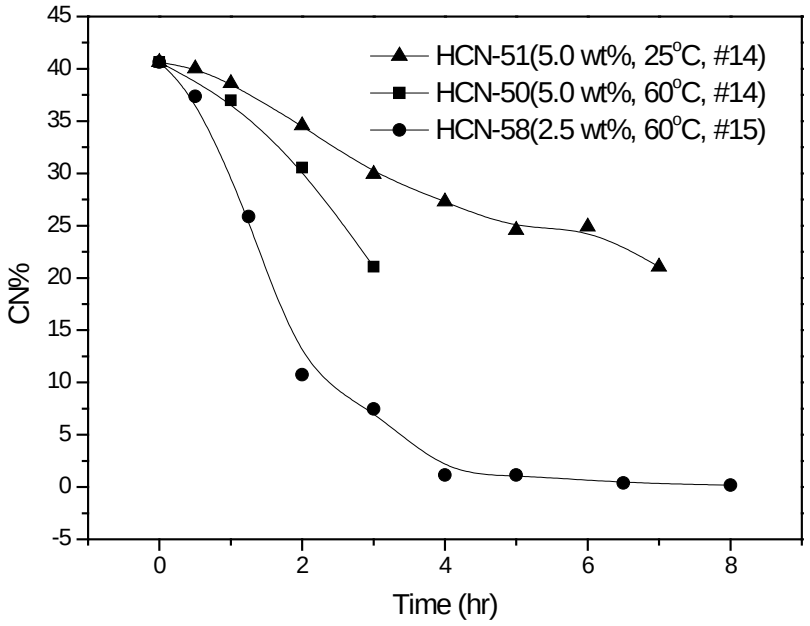


Figure 7-4 Hydrogenation of C≡Ns in NBR of different concentration

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100 ml 2.5 wt% NBR in THF, 500 psig

Since positive results were obtained for hydrogenation of nitriles in a THF solution of 2.5 wt% NBR, efforts were made to increase the concentration to a higher level. However increasing the NBR concentration did not result in a faster reaction but caused more severe cross-linking. It seems that higher rubber content causes more gel formation, because there are more polymer chains in a more concentrated NBR solution; as a result, when the nitrile group is broken in the presence of the Rh catalyst, C-N or C=N radicals will have more chance to encounter other polymer chains which will be tangled together and cause cross-linking. 2.5 wt% NBR solutions in THF have been used through this research.

7.3.1.5 Effect of Solvent

The result for nitrile hydrogenation of NBR in various solvents is much the same as in the hydrogenation of nitriles of HNBR. In most of the experiments in this thesis, THF was selected as the solvent, because THF is not only a good solvent for nitrile butadiene rubber, but for the catalyst being

used as well. Other than THF, different solvents have also been investigated, such as MEK, acetone and MCB. However none of these were found to work for current system. In fact, the catalyst being used does have some reactivity in toluene; however toluene is not a good solvent for butadiene rubbers, so not much work has been carried out in toluene.

7.3.1.6 Effect of Agitation

As is well known, for a homogeneous catalytic system, dispersion of the catalyst should not be a problem because homogeneous catalysts dissolve in the solvent quickly and completely. Some experiments were carried out to confirm the above point. In Figure 7-5 and Figure 7-6, different agitation speeds and agitation type have been investigated. The anchor stirrer used in the present work is shown in Figure 7-7. The results clearly show that there is no large difference whatever agitation speed or stirrer type is used.

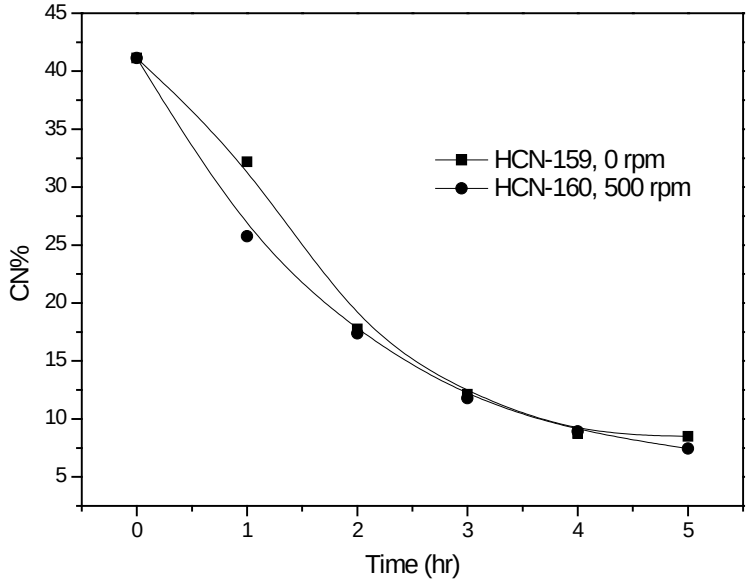


Figure 7-5 Effect of agitation speed on hydrogenation of C≡Ns in NBR

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100 ml 2.5 wt% NBR in THF, 60^{o}C, 500 psig

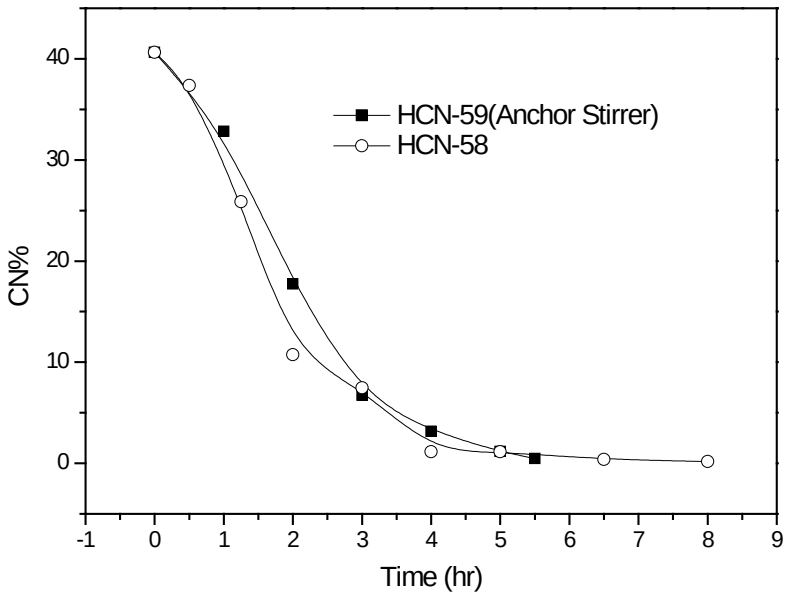


Figure 7-6 Effect of stirrer type on hydrogenation of C≡Ns in NBR

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100 ml 2.5 wt% NBR in THF, 60^{o}C, 500 psig

Figure 7-7 Anchor stirrer manufactured by Parr Instrument Inc.

7.3.2 Tandem Hydrogenation of Nitrile and Olefinic Groups in NBR and the Preliminary Study of the Reaction Mechanism

Obviously, the catalyst being used, $RhH(P^iPr_3)_3$, has great potential for the reduction of nitriles in NBR. Moreover, this Rh hydrido complex hydrogenates carbon-carbon double bonds at the same time. Figure 7-8 shows that, $RhH(P^iPr_3)_3$ reduces the nitrile percentage from 40% to <10% within 5 hours, and increases the hydrogenation degree of C=Cs to >90% at the same time. As stated in chapters 1 and 2, the main goal of this study is to reduce the nitrile group (acrylonitrile content) in HNBR or NBR; fortunately, $RhH(P^iPr_3)_3$ is also active for hydrogenating unsaturated carbon-carbon bonds. Since the technology of olefinic hydrogenation of butadiene rubbers has already been commercialized decades ago, and the activity and efficiency of its catalyst are both higher than the catalyst used in the present study, an extensive investigation was not conducted as was carried out for nitrile reduction.

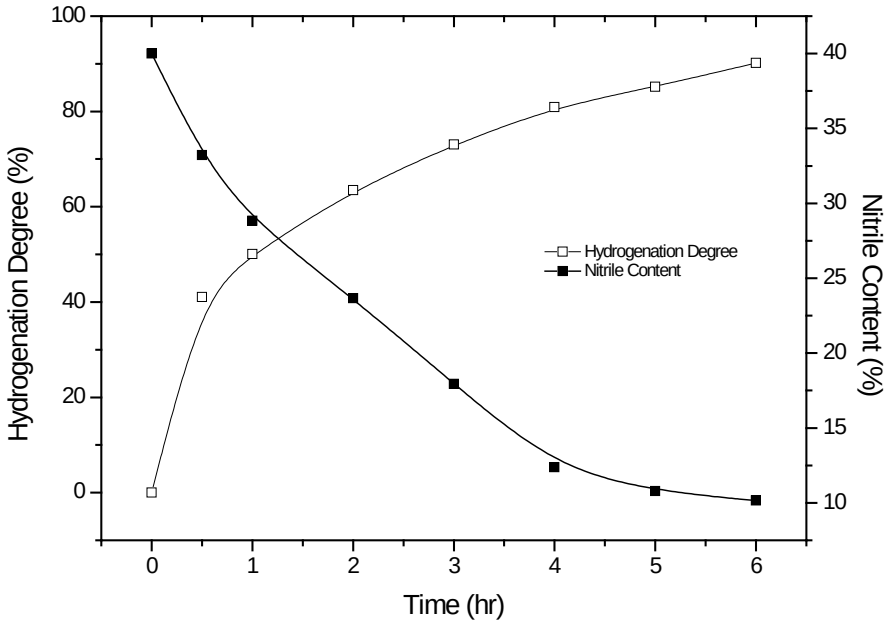


Figure 7-8 Tandem hydrogenation of C=Cs and C≡Ns in NBR

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100 ml 2.5 wt% NBR in THF, 60^{o}C, 500 psig

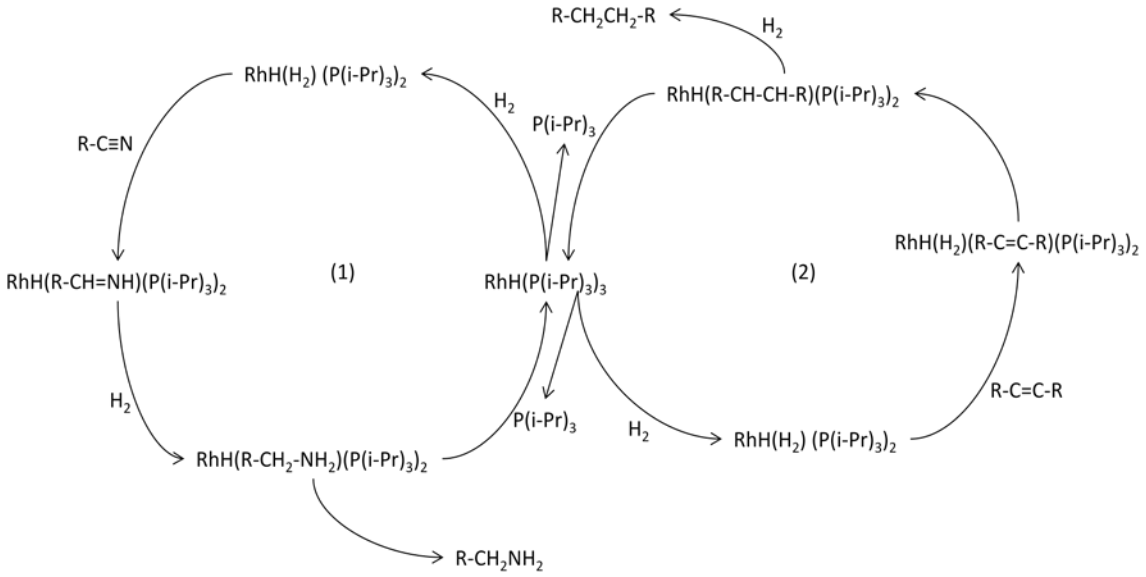


Figure 7-9 Possible mechanism for tandem hydrogenation of nitrile and olefinic groups in NBR

A possible reaction mechanism shown in Figure 7-9 is proposed for the first time in this study for the tandem hydrogenation of nitriles (1) and olefins (2) in nitrile butadiene rubber (NBR). Hydrogenation is performed under 500 psig at 60^{o}C using tris(triisopropylphosphine)hydrido-rhodium(I). It is not entirely certain as to which reaction occurs, however this seems to be a plausible mechanism.

Wilkinson's Catalyst is a widely studied catalyst known to selectively hydrogenate olefins in acrylonitrile butadiene copolymers (NBR).[20] The catalyst being used in the present study, tris(triisopropylphosphine)-hydridorhodium(I), has been shown to hydrogenate both the nitrile groups and olefins of NBR, and thus the mechanism has been split into two parts. Part 2, as labeled in Figure 7-9 displays the hydrogenation of olefins. It is believed that hydrogenation due to this catalyst is very similar to the mechanism proposed by Parent, *et al.*[20] as shown below in Figure 7-10.

The addition of hydrogen to the catalytic complex (first step of both parts) has also been reported by Yoshida, *et al.*[35,36] This addition creates a new five-member catalyst complex. A similar five-member complex with two chlorine atoms instead of two hydrogen atoms has been reported by Butler *et al.*[110] Furthermore, Parent, *et al.*[20] reported that Wilkinson's catalyst $RhCl(PPh_3)_3$ can form a five-member complex with two hydrogen atoms under similar conditions to those used in the present study. Thus the complex proposed above is not unreasonable and is a likely step in the catalysis of the hydrogenation reactions.

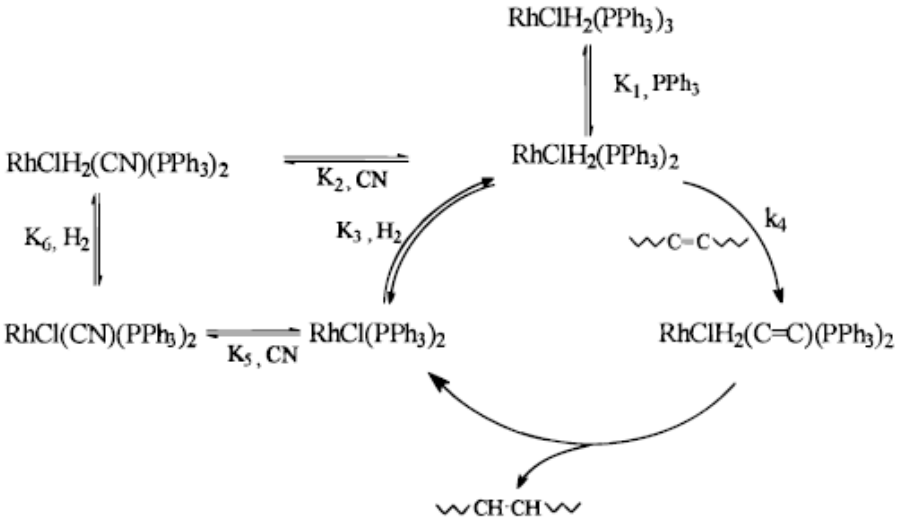


Figure 7-10 Mechanism for olefin hydrogenation using Wilkinson's catalyst[20]

The next step is a little more difficult to determine. A likely mechanism for this part of the reaction involves the rhodium complex reacting with the C≡N bonds along with hydrogen gas to reduce the nitrile to an amine. Similar additions to double and triple bonds were noted in a thesis paper by Lau,[127] further supporting the proposed reaction mechanism. Finally, Parent *et al.*[20] mentioned that "a highly significant $[H_2]$*[CN] interaction operates within the kinetic mechanism." It seems highly likely that the rhodium catalyst being used in this study reacts with the C≡N bonds in much the same way; both this rhodium catalyst and Wilkinson's catalyst reduce olefins in polymers in the presence of hydrogen under high pressure and temperature.

7.3.3 Gel Formation

Based on the results above, visible gel formation is observed during the reaction and it seems to be inevitable for the reduction of nitriles in diene-based polymers like NBR and HNBR. Especially when C≡N% drops below 30%, severe gel formation might occur. In order to completely solve or minimize the gel formation issue, many attempts have been made which will be discussed below.

One goal of this project is to reduce the percentage of nitrile by 5%-10%, and the current catalyst is reacting too fast to meet this requirement. Thus the addition of some additives to terminate the hydrogenation may be an option worth considering. A variety of chemicals have been assessed and the results are shown in Table 7-1. In summary, acetic acid, ethanol and MCB terminate the reaction immediately, but visible gel is still observed. MEK and TEMPO only slow down the reaction and do

not seem to reduce the gel formation. TEMPO is also called 2,2,6,6-tetramethyl-1-piperidinyloxy or 2,2,6,6-tetramethylpiperidine 1-oxyl and is a commonly used free radical.

Table 7-1 Summary of additives for gel formation reduction

	Hydrogenation of C≡N	**Hydrogenation of C=C**	**Gel Formation**
Acetic acid	Terminated	Terminated	Rubber coagulated
Ethanol	Terminated	Terminated	Visible gel
MCB	Terminated	Terminated	Visible gel
MEK	Slower	Slower	Visible gel
TEMPO	Slower	Slower	Visible gel
TPP	Terminated	Not terminated	No visible gel

However it was found that triphenylphosphine (TPP) seems to be a very good additive to reduce or minimize gel formation. First, TPP is able to terminate the hydrogenation of the nitrile group, and it does not affect the hydrogenation of carbon-carbon double bonds. Secondly, and the most important thing is that no visible gel is observed when adding TPP.

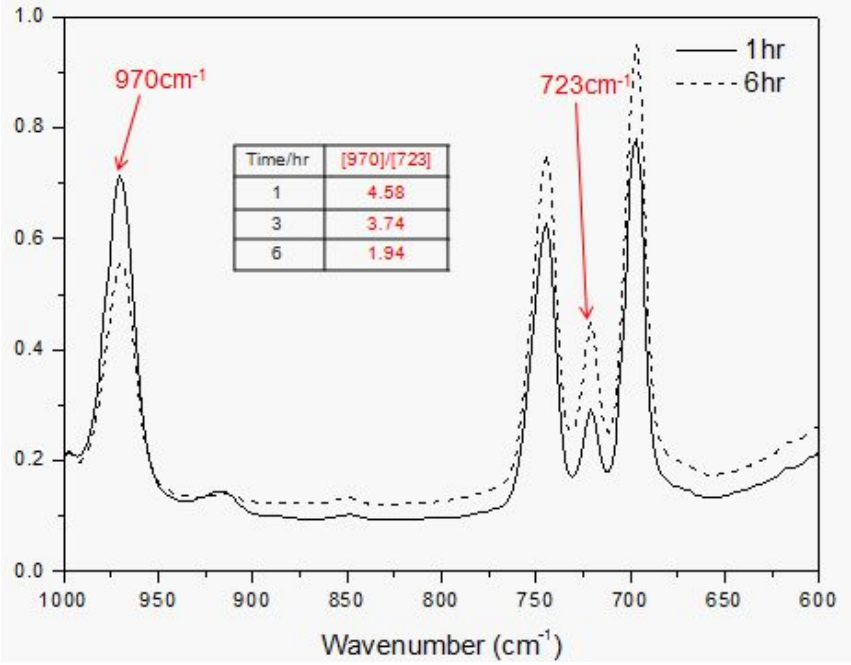


Figure 7-11 FT-IR spectrum of hydrogenation of C≡Ns in NBR with TPP

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100ml 2.5 wt% NBR in THF, 60^{o}C, 500 psig

Actually, adding TPP into the system makes it very difficult to calculate the content of nitrile groups due to the two peaks generated by TPP besides the peak of the methyl group at 723 cm^{-1} in FT-IR spectrum (shown in Figure 7-11). As a result, in order to determine if hydrogenation of C=Cs is really terminated or not, the peak height of 970 cm^{-1} ($=CH_2$) and 723 cm^{-1} ($-CH_3$) were compared, and the results are shown in Figure 7-11. The ratio of [970]/[723] decreases from 4.58 to 1.94 after 6 hours, which means C=Cs continue to be reduced to C-C after addition of TPP.

Based on the fact that hydrogenation of nitriles is terminated and that of carbon-carbon double bonds is not, TPP plays a crucial role in the process. Regarding the function of TPP, the following dynamic equilibrium has been proposed and is quite likely,

$$RhH(P^iPr_3)_3 + PPh_3 \longleftrightarrow RhH(PPh_3)_4 + P^iPr^3$$

As shown above, when TPP is added, TPP ligands start replacing $PiPr_3$ ligands of the Rh hydrido complex until equilibrium is reached. This explains why hydrogenation of nitriles is terminated. The new catalyst, $RhH(PPh_3)_4$, has already been shown to be a very effective catalyst for the hydrogenation of C=Cs.[20] Although, it seems that things are quite well explained by this equilibrium, more investigation of the mechanism is still required in the future. With respect to factors causing gel formation, the major factor might be the breaking of C≡N triple bonds which generates many radicals that may interact with the free polymer chains. In addition, P^iPr_3 ligands may also contribute to the cross-linking. More details about gel formation have also been discussed in Chapter 6.

7.3.4 Characterization

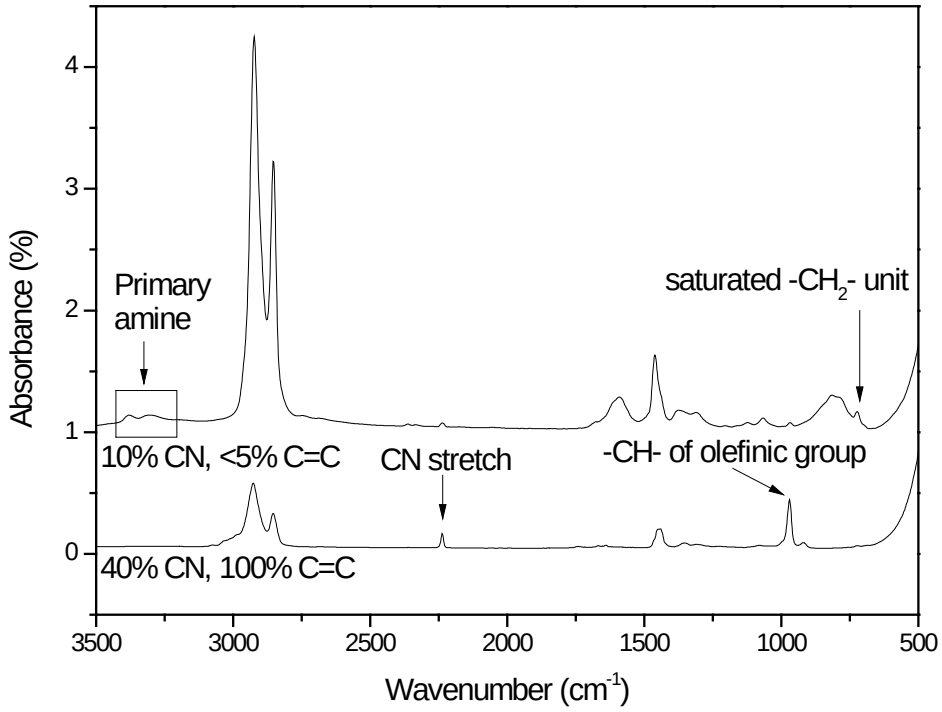


Figure 7-12 FT-IR spectra of hydrogenation of nitrile and olefinic groups in NBR

Figure 7-12 clearly depicts the FT-IR spectra of the hydrogenation of the nitrile and olefinic groups in NBR at different conversions. Similar to the case of hydrogenation of nitrile groups in HNBR, the peaks at 2236 cm^{-1} and 723 cm^{-1} belong to -C≡N and saturated -$[CH_2]_n$- unit (n > 4), respectively. Since this is an NBR system, there are peaks for unsaturated carbon-carbon bonds in the 920-1000 cm^{-1} region before hydrogenation. During the hydrogenation reaction, the ν(C≡N) decreases and two bumps appear at 3200-3400 cm^{-1} which are the classic peaks of primary amines. No secondary amines or other types of amines (widely reported side products) are observed. At the same time, the peak of the unsaturated carbon-carbon bond at around 1000 cm^{-1} significantly decreases and the peak of saturated -$[CH_2]_n$- unit starts to show up at 723 cm^{-1}. In the end, the unsaturated carbon-carbon bond peak (1000 cm^{-1}) and nitrile peak (2236 cm^{-1}) almost disappear when the carbon-carbon double bond content is more than 95% and the nitrile content is about 10%, which means the catalyst is highly effective for tandem hydrogenation of olefinic and nitrile groups in NBR. The new peak for the

primary amines (3200-3400 cm^{-1}) confirms that nitrile groups have been successfully converted to amine groups without any side products.

7.4 Conclusions

In this chapter, the tandem hydrogenation of nitrile group and olefinic groups in NBR has been investigated, and it has been shown that $RhH(PPr^{i}_{3})_3$ is an very effective catalyst. This is the first report of the development and establishment of a catalytic system that is able to conduct tandem hydrogenation of both nitrile groups and olefinic groups in butadiene rubbers (macromolecules) without visible gel formation. The nitrile content can be reduced from 40% to less than 10% and the olefinic groups have been reduced from 100% to lower than 5% at the same time, and it takes less than 5 hours under relatively mild conditions ($60^{o}C$ and 500 psig H_2). The nitrile groups have been converted to primary amines. A possible mechanism for tandem hydrogenation has also been proposed for the first time. Gel formation issues exist during the regular procedure, and temperature and catalyst concentration seem to aggravate gel formation. The causes for gel formation during nitrile reduction have been investigated and a potential mechanism was also proposed. Some additives have been tested and some of them are found to be able to slow down or terminate the gel formation, among which TPP is the most effective one.

Chapter 8
Hydrogenation of Olefinic Groups in SBR

8.1 Introduction

Styrene Butadiene Rubber (SBR) is one of the most widely used synthetic rubbers in the world. This copolymer has good strength, outstanding resilience, and high elongation at break.[130] It has been used in various industrial applications, including manufacture of tires, wire and cable insulation, shoe soles, adhesives, membranes, belts and hoses, toys, surgical and sanitary products.[131] However, SBR has poor aging properties due to the presence of unsaturated carbon-carbon double bonds (C=Cs) in its butadiene segment.[132] An improved method is to hydrogenate the double bonds.[133] Hydrogenated styrene butadiene rubber (HSBR) exhibits improved thermal, oxidation, ozone and UV (ultraviolet) resistance.[134] These properties allow HSBR to be used in extended applications which includes the abovementioned applications as well as other applications that require more weather and temperature resistance.[135-138]

Recently, several catalysts have been reported to be able to hydrogenate SBR effectively. Barrios *et al*. utilized a Ziegler-Natta type catalyst made from a reaction between NiAcAc and n-Buli to selectively hydrogenate 1,2-vinyl and 1,4-trans bonds in a styrene-butadiene copolymer.[139] Holleben *et al*. proposed a way to hydrogenate SBR using a Pd/C catalyst with limonene as a hydrogen source.[140] Jamanek *et al.* provided a hydrogenation process using monocyclopentadienyl titanium(IV).[135] He *et al.* claimed that group VII metal carboxylates with one or more aluminum alkyls are useful hydrogenation catalysts[134] whereas Dath *et al.* favored a catalyst with at least one group Ia, Ib, IIb, VIb, VIIb or VIII metal on support of an alkaline earth metal silicate.[141]

Some main concerns in the hydrogenation of SBR is in minimizing the amount of catalyst metal residue left in the products[142] as well as in preventing cross-linking.[133] The presence of metal residue might arise in product contamination and limit its use.[143] Ko *et al*. described a process to remove metal catalyst in hydrogenated polymer solution from around 200 ppm to 5-10 ppm.[142] Yet, metal residue removal is a costly process. The removal requires expensive metallurgy due to the corrosive nature of the compound consisting of the catalyst or formation of acid salts in the process, and may involve multiple stages or further treatment.[143] Hence, it is essential to use an efficient catalyst which can be used in small amount to hydrogenate SBR in a reasonable time such that removal of metal catalyst becomes unnecessary.

During the investigation of hydrogenation of nitrile groups and olefinic groups in butadiene polymers, it was found that the Rh hydrido complex being used for nitrile reduction can also remove the carbon-carbon un-saturation in SBR and shows very good performance. Since it is the not main task, not many experiments were carried out; however some promising results have still been obtained which will be discussed in this chapter.

8.2 Experimental

8.2.1 Materials

For the detailed information of the chemicals used in this chapter, please refer to section 3.2.1.

8.2.2 Equipment

The main equipment used in this work has been described previously, please refer to section 3.2.2.

8.2.3 Characterization

In order to determine the conversion of carbon-carbon double bonds in the hydrogenation reaction, samples are taken at certain time intervals during the experiments. A Bio-Rad FTS 3000MX spectrometer and a Thermo Nicolet 6700 spectrometer were used for Fourier transform infrared (FT-IR) analysis of samples. The degree of hydrogenation was calculated based on the method developed by Marshall *et al.*[86,144,145] and modified by De Sarkar *et al.*[146,147] A967, A909 and A699 represent the absorbance values of trans, vinyl, cis, and styrene units at 967, 909 and 699 cm^{-1}, respectively. As the aromatic ring of the styrene unit is unaffected during hydrogenation, the 699 cm^{-1} peak serves here as the internal standard. The detailed calculation is listed below:

$$A699 = absorbance\ at\ 699\ cm^{-1}$$
$$A910 = absorbance\ at\ 910\ cm^{-1}$$
$$A967 = absorbance\ at\ 967\ cm^{-1}$$

$$A(910) = \frac{A910}{A699}\ and\ A(967) = \frac{A967}{A699}$$

$$K(910) = 1.7635, a\ constant\ specific\ to\ this\ peak$$
$$K(967) = 0.4717, a\ constant\ specific\ to\ this\ peak$$

$$\boldsymbol{Degree\ of\ Hydrogenation}\ (\boldsymbol{mol}\ \%) = 1 - \left(\frac{A(910) \times 50\%}{K(910)} + \frac{A(967) \times 50\%}{K(967)}\right) \times 100\%$$

For other information, please refer to section 3.2.3.

8.2.4 Hydrogenation Procedure

Solutions of SBR (2.5 wt%) in tetrahydrofuran (THF) were initially prepared and placed on a shaker for one day to allow for the complete dissolution of rubber.

The detailed information of experimental procedure has been described previously, please refer to section 3.2.4.

8.3 Results and Discussion

8.3.1 Effect of Different Experimental Conditions

8.3.1.1 Effect of Temperature

In Figure 8-1 the effect of temperature on the hydrogenation of SBR is clearly shown. From 60^{o}C to 120^{o}C, since there is more energy for molecules to move faster, the final hydrogenation degree of C=C increases from to 60% to 93% after reacting for 5 hours. However further increasing temperature does not improve the performance. Instead, when the temperature is as high as 140^{o}C or higher, the reactivity of the catalyst does not increase much or even drops to a lower level. There are two possible causes: firstly, the high temperature causes the rubber solution to become unstable. According to published literature regarding SBR hydrogenation, the highest temperature reported is 160^{o}C; there is some coagulation of SBR observed when the temperature is higher than 120^{o}C. Secondly, the catalyst being used is not very stable under high temperature such as 140^{o}C or higher. $RhH(PPr^{i}_{3})_3$ might be deactivated at such a high temperature as reported by Yoshida *et al.*[35,36,120] One thing that needs to be pointed out is that there is no gel formation observed during and after the hydrogenation process.

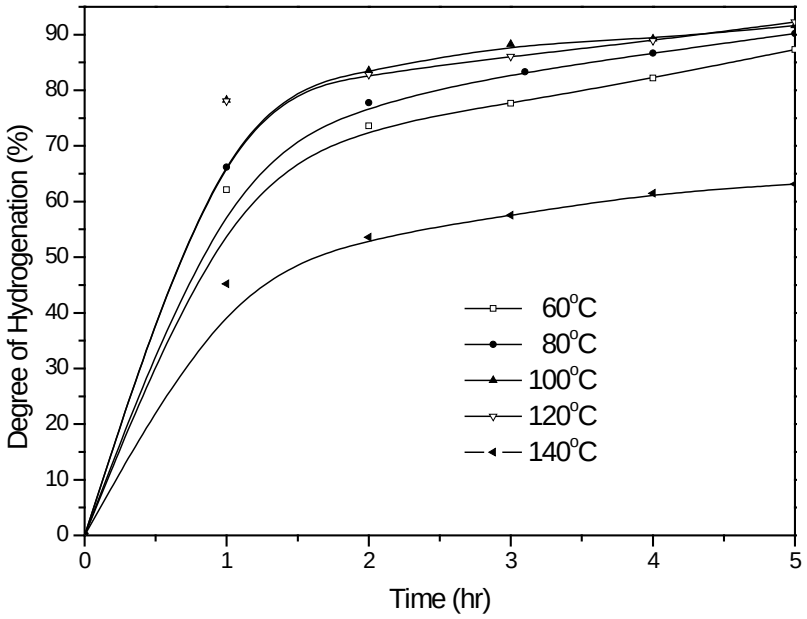


Figure 8-1 Effect of temperature on the hydrogenation of SBR

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100 ml 2.5 wt% SBR in THF, 500 psig

8.3.1.2 Effect of Catalyst Loading

Figure 8-2 clearly shows that the reaction occurs faster by increasing the amount of catalyst added from 0.025 mmol to 0.125 mmol, especially from 0.05 mmol to 0.075 mmol. This can be explained that there are more C=C bonds at the surface of SBR particle and they are the easiest to be hydrogenated, more catalysts will remove those unsaturated bonds on the surface much faster. When 0.125 mmol catalyst was added, the degree of hydrogenation was almost 95% within 4 hours. However, on adding a greater amount of catalyst into the system, the hydrogenation process did not proceed any faster, which probably can be explained in that it is harder or impossible for excess catalyst to be transported into the SBR particles. It was also found out that a high Rh/rubber ratio (rhodium amount > 0.2 mmol) may cause rubber coagulation during the experiment, which could be caused by excessive rhodium salt; a similar phenomenon was observed in hydrogenation of NBR latex which was discussed in Chapter 4. Again, no gel formation or coagulation was observed during the regular hydrogenation process.

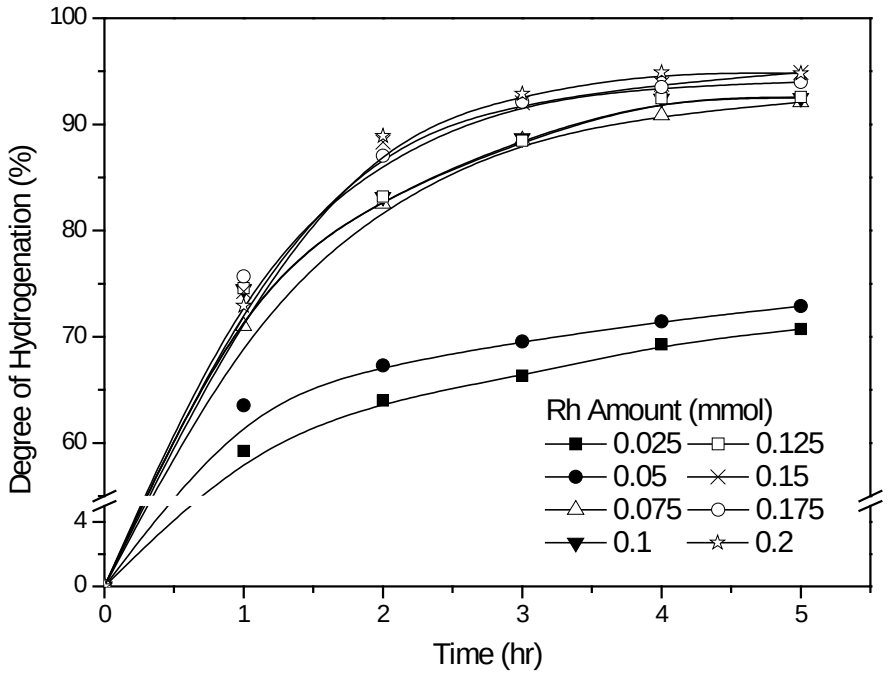


Figure 8-2 Effect of catalyst loading on the hydrogenation of SBR

100 ml SBR in THF (2.5 wt%), 60^{o}C, 500 psig, 250 rpm

8.3.1.3 Effect of Hydrogen Pressure

The influence of hydrogen pressure on the SBR hydrogenation reaction was also examined. Figure 8-3 shows that the degree of hydrogenation decreases as the hydrogen pressure decreased. It seems that H_2 pressure does have some effect on the hydrogenation of carbon-carbon double bonds in SBR using this rhodium hydrido complex, because the higher H_2 pressure results in a higher concentration of H_2 in the aqueous phase and makes hydrogenation of carbon-carbon double bonds easier. However, it is worthwhile to mention that the hydrogenation degree only varies from 90% to 96% when the hydrogenation pressure is between 300 psig and 1100 psig; therefore, it may be concluded that the hydrogenation rate is mainly controlled by the catalyst mass transfer within SBR particles, which is similar in most of the present cases.

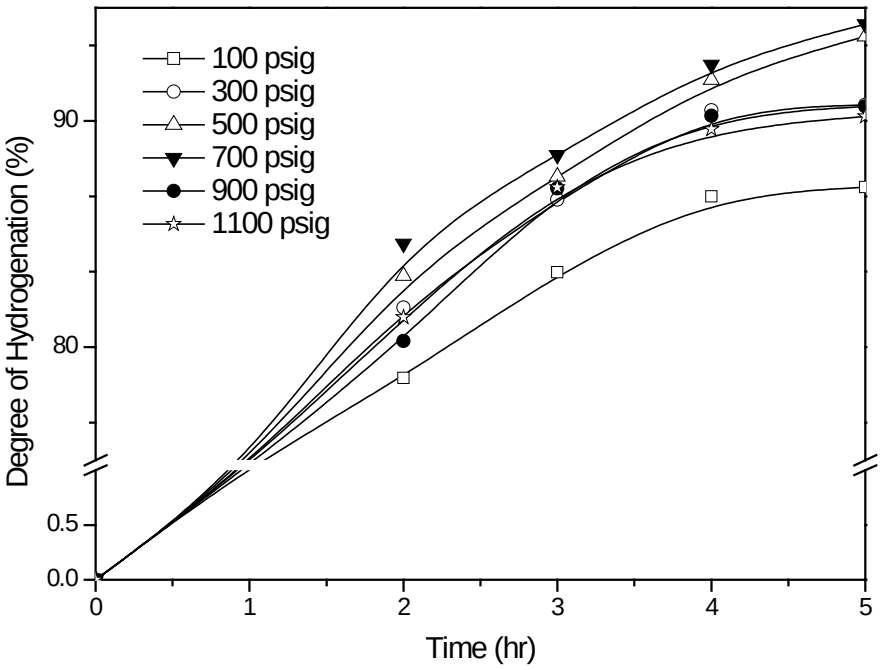


Figure 8-3 Effect of hydrogen pressure on the hydrogenation of SBR

0.8 ml catalyst solution (0.06 g catalyst, 0.1 mmol Rh), 100 ml SBR in THF (2.5 wt%), 60^{o}C

8.3.2 Preliminary Study of the Reaction Mechanism

The technology of hydrogenation of SBR has been widely studied and thoroughly understood. A possible reaction mechanism using $RhH(PPr^{i}_{3})_3$ shown in Figure 8-4 is proposed for the hydrogenation of olefins in styrene butadiene rubber (SBR). This mechanism is based on those found in the literature for similarly structured complexes.[3,100,126] The family of $RhClPR_3$ and $RhHPR_3$, where R represents different ligands, has been widely studied. The most well-known of these being Wilkinson's Catalyst (R = PPh_3). It has been theorized that all catalysts of this type react in the same way to hydrogenate olefins in both small molecules and in polymers. Figure 8-5 describes this mechanism using "L" to indicate the ligand and "sol" to indicate molecules in the solution that the reaction takes place in.

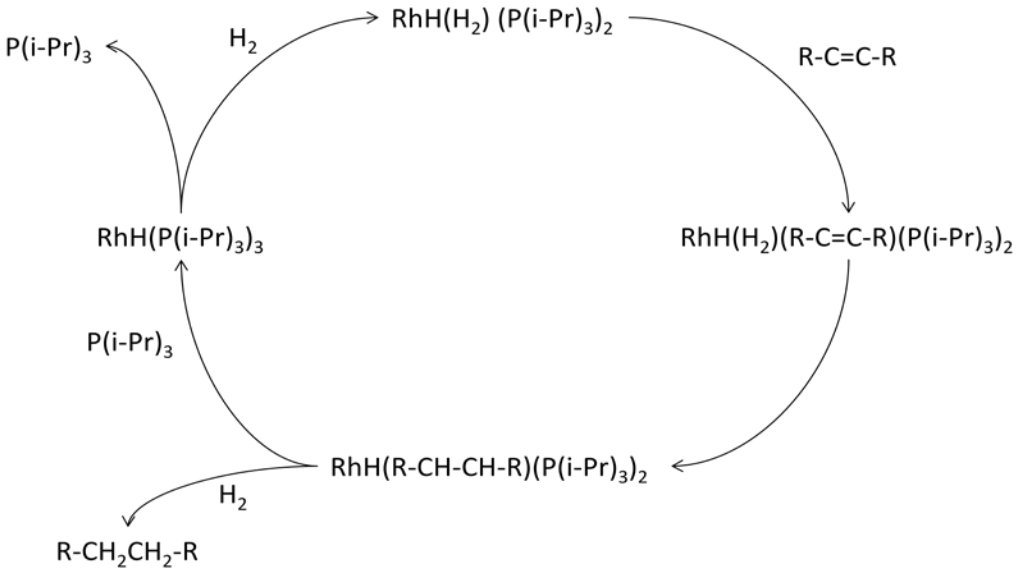


Figure 8-4 Possible mechanism for the hydrogenation of SBR using $RhH(P(i\text{-}Pr)_3)_3$

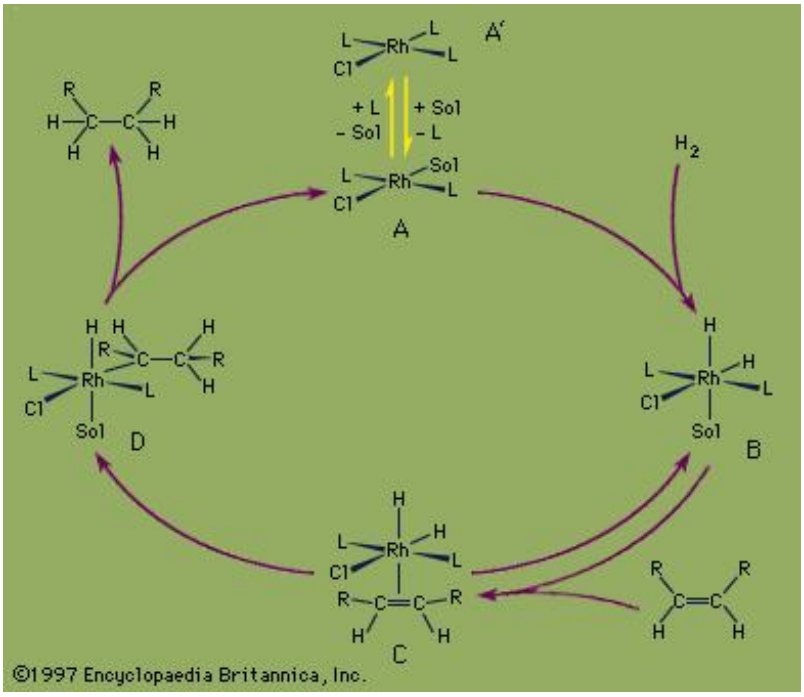
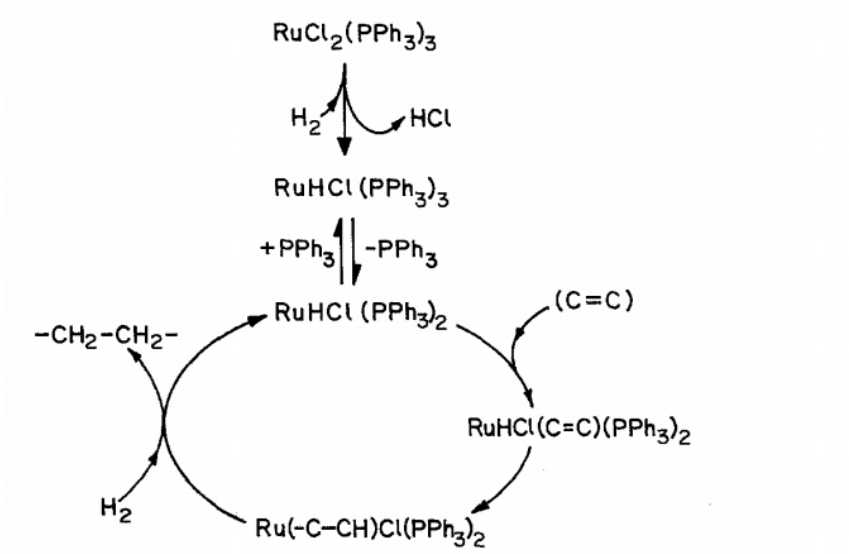


Figure 8-5 Mechanism for olefin hydrogenation according to the Britannica Encyclopedia

Singha *et al.*[100] reported a similar mechanism taking place using a ruthenium-based Wilkinson catalyst. Figure 8-6 shows this mechanism and how the structure of the molecule is very similar to that of $RhH(P(i\text{-}Pr)_3)_3$. The reaction is for hydrogenation of SBR.



Scheme-1. Catalytic cycle of hydrogenation of SBR using $RuCl_2(PPh_3)_3$

Figure 8-6 Mechanism for catalytic hydrogenation of SBR using $RuCl_2(PPh_3)_3$[100]

The mechanisms shown and the reactions proposed also hold true for the hydrogenation of NBR using the same catalyst. For the mechanism for NBR system please refer to Chapter 4 and Chapter 6. The main difference between SBR and NBR hydrogenation is the lack of nitrile groups in SBR. Selectivity can also arise in SBR between the internal and vinyl C=C.[3]

8.3.3 Characterization

8.3.3.1 FT-IR

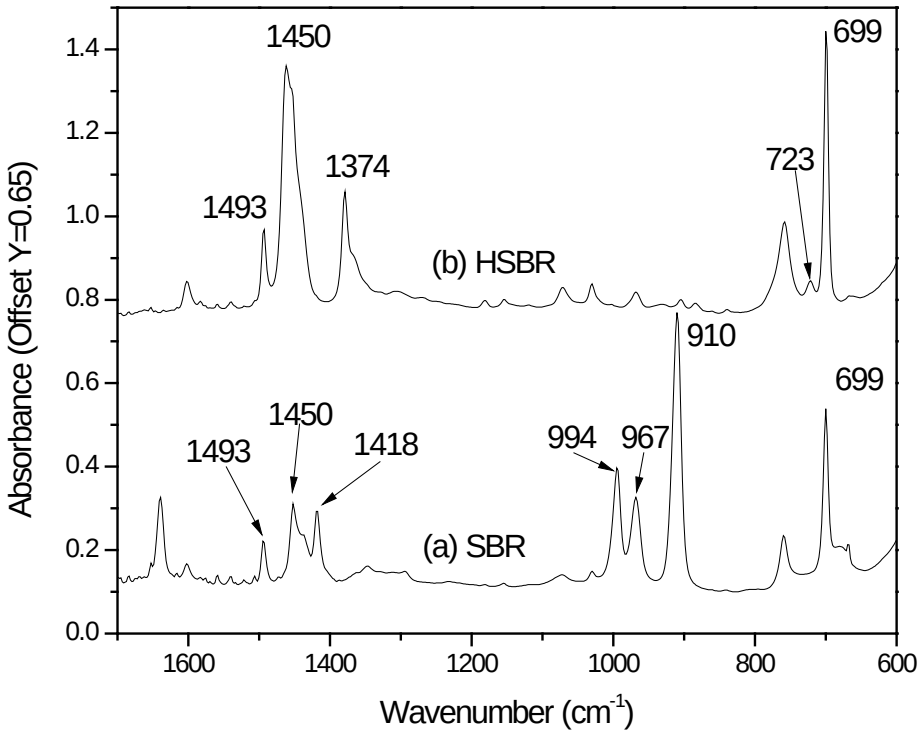


Figure 8-7 IR spectra of SBR (a) and HSBR (b)

FT-IR spectra of SBR and HSBR are shown in Figure 8-7. The spectrum of SBR indicates peaks at 699 cm^{-1} due to the styrene unit, 757 cm^{-1} due to 1,4-*cis*, 910 cm^{-1} due to 1,2-vinyl, and 967 cm^{-1} due to 1,4 *trans* unsaturated units. As the level of hydrogenation increases, the peak at 910 cm^{-1} (attributed to vinyl -CH_2-), and the peaks at 967 and 994 cm^{-1} (assigned to -CH- trans units) have disappeared in Figure 8-7(b) compared to Figure 8-7(a), and the peak at 1450 cm^{-1} due to the -CH_2- deformation vibration increases. The disappearance of all characteristic absorbencies of C=C suggests nearly quantitative hydrogenation of the C=C bonds. A new peak at 723 cm^{-1} for cis-1,4 saturated units appears in the spectra of the hydrogenated SBR samples, which has been significantly overlapped by the peak at 699 cm^{-1} for styrene. A peak at 1374 cm^{-1} due to the deformation vibration of the -CH_3 group is also clear in the spectra of HSBR due to the reduction of the pendent vinyl group. Two peaks at 2852 cm^{-1} and 2925 cm^{-1} due to the -CH- stretching vibration of the -CH_2- group

(methylene) increase with an increase in the level of hydrogenation. The absorption peak at 699 cm^{-1} shows no change in intensity, reflecting that the aromatic ring of the styrene unit is not reduced under the given hydrogenation conditions. The retention of the same intensity of the characteristic absorbance for aromatic rings at 699, 1450 and 1493 cm^{-1} indicates that the hydrogenation is highly selective toward olefinic bonds.

8.3.3.2 NMR

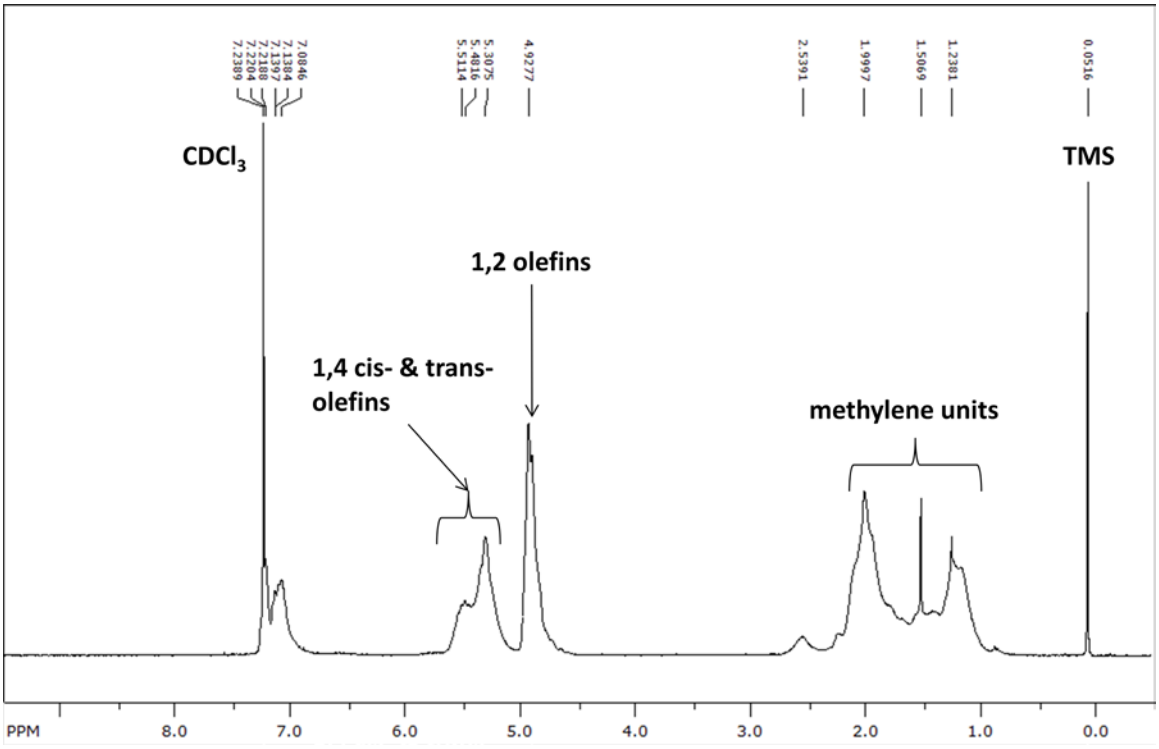


Figure 8-8 ^{1}H-NMR spectra of SBR

Figure 8-8 and Figure 8-9 show the representative ^{1}H-NMR spectra of the control and the partially hydrogenated SBRs. Major peaks are observed in the aliphatic (0.5–2.8 ppm) and olefinic (4.6–5.8 ppm) regions. Aromatic protons show peaks in the region of 6.8–7.2 ppm. Detailed assignment of the NMR peaks is shown in Table 8-1. There is no change in intensity of the peaks due to styrene, reflecting the stability of the aromatic ring toward hydrogenation. With the progress of hydrogenation, the olefinic peak area decreases considerably. Concurrently, a peak at 1.25 ppm assigned to the methylene sequence increases with increase in the hydrogenation of the double bonds. The peak at 4.99 ppm due to the 1,2-butadiene unit is almost absent from the spectrum of

hydrogenated SBR, indicating that 1,2-butadiene units are more rapidly hydrogenated than are 1,4 units. This is in accord with the IR results discussed above.

Table 8-1 Peak assignments for SBR ^{1}H-NMR spectra[148-150]

Chemical Shifts (ppm)	Assignments
0.05	Tetramethylsilane (TMS)
0.8-1.5	Different existing microstructure for SBR
2.0	-CH_2- from styrene and trans-1,4-butadiene
2.5	Styrenic -CH-
4.9	=CH_2 (olefinic hydrogen of 1,2 unit)
5.3-5.5	-CH=CH- and –CH=CH_2 cis- and trans-1,4 units
7-7.24	H attached to the aromatic ring
7.24	$CDCl_3$

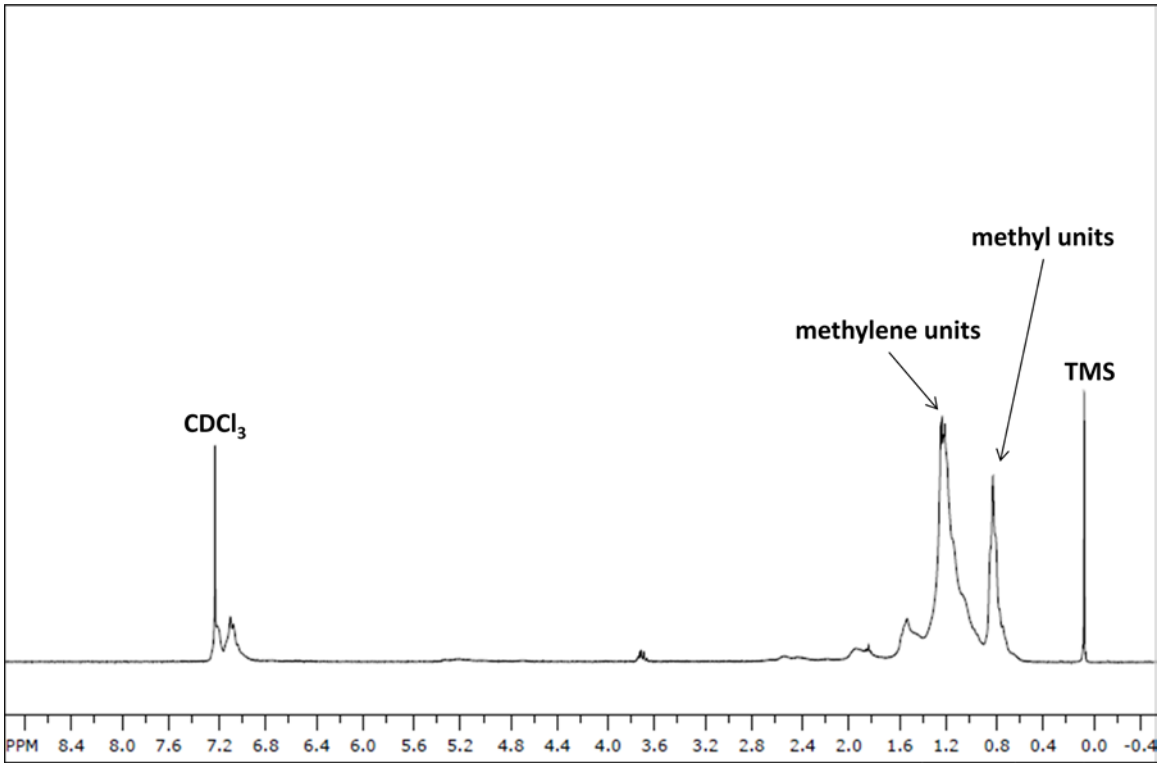


Figure 8-9 ^{1}H-NMR spectrum of HSBR

8.4 Conclusions

An effective catalytic system for the hydrogenation of carbon-carbon double bonds in SBR was successfully developed. In the absence of any additives, the C=C bonds in SBR were hydrogenated by using $RhH(P(i\text{-}Pr)_3)_3$ to more than 95% in a relatively short period of time and no obvious cross-linking was observed. Optimization of experimental conditions has been carried out for eco-friendly and energy saving purposes. The effect of catalyst/polymer ratio, polymer concentration, reaction temperature (60-160^{o}C) and hydrogen pressure (100-1200 psig) on activity of the catalytic system have been studied. The properties of SBR did not change after hydrogenation of the unsaturated C=C bonds. This study provides a new route not only in chemical modification of SBR by using a rhodium complex but in hydrogenation of other unsaturated polymers such as diene-based rubbers.

Chapter 9

Conclusions and Recommendations for Future Research

9.1 Conclusions

The conclusions of this thesis are summarized and listed below.

9.1.1 Hydrogenation of Olefinic Groups in NBR Latex

NBR in the form of latex has been successfully hydrogenated to high conversion by using $RhCl_3$ without any organic solvent. NBR latex can be hydrogenated to a degree of more than 95% within 5 hours at 160^{o}C using $RhCl_3$ in the presence of TPP as the co-catalyst. Wilkinson's catalyst is synthesized *in situ* during hydrogenation. The catalyst for latex hydrogenation should be defined as $RhCl_3$/TPP. TPP is also a catalyst mass transfer promoter and reducing agent. Ethanol is a very effective co-solvent for TPP and $RhCl_3$ (but not for the rubber), and significantly improves in situ synthesis of Wilkinson's catalyst.

9.1.2 Hydrogenation of Nitrile Groups in HNBR

$RhH(PPr^{i}_{3})_3$ is capable of hydrogenating nitrile groups in HNBR. The nitrile content can be reduced from 40% to less than 10% within 5 hours at 60^{o}C and 500 psig H_2, without any visible gel formation. The nitrile groups have been converted to primary amines without any side product. A possible mechanism for nitrile hydrogenation has been proposed. Gel formation issues exist during regular hydrogenation procedures, and the causes for gel formation during nitrile reduction have been investigated and a potential mechanism was proposed. Some additives were found to be effective to slow down or terminate the gel formation, and TPP is the most effective one. During the hydrogenation, TPP replaces the ligand of the catalyst and produce another Rh hydrido complex.

9.1.3 Tandem Hydrogenation of Nitrile and Olefinic Groups in NBR

The tandem hydrogenation of nitrile group and olefinic groups in NBR has been achieved by using $RhH(PPr^{i}_{3})_3$. The nitrile content can be reduced from 40% to less than 10% and the olefinic groups has been reduced from 100% to lower than 5% simultaneously, and it takes less than 5 hours under relatively mild conditions (60^{o}C and 500 psig H_2). The nitrile groups have been converted to primary amines without any side product. A possible mechanism for nitrile reduction has also been proposed for the first time. A potential mechanism for gel formation was also proposed. Some additives are

found to be able to slow down or terminate the gel formation, among which TPP is the most effective one. During the hydrogenation, TPP replaces the ligand of the cataslyt and produce another Rh hydrido complex which is able to continue the hydrogenation of carbon-carbon double bonds alone.

9.1.4 Hydrogenation of Olefinic Groups in SBR

An effective catalytic system for the hydrogenation of carbon-carbon double bonds in SBR was successfully developed. In the absence of any additives, the C=C bonds in SBR were hydrogenated by using $RhH(P(i\text{-}Pr)_3)_3$ to more than 95% in a relatively short period of time and no obvious cross-linking was discovered. The properties of SBR did not change after hydrogenation of the unsaturated C=C bonds.

9.1.5 Milestones and Contributions

As a result of this research project, a rhodium hydrido complex was screened and successfully synthesized; a corresponding catalytic system was therefore established. The nitrile group in NBR and HNBR has been selectively hydrogenated to primary amines without any side product. Moreover, realization of tandem hydrogenation of nitrile and olefinic groups in butadiene rubber brings the possibility of tandem vulcanization and hydrogenation in butadiene rubber or other types of polymers in the future.

Based on the current achievement, a successful $RhCl_3$/TPP catalyst system for NBR hydrogenation in the latex form has been initially developed which fulfills all major requirements (listed in section 3.1) for developing an organic solvent-free polymer latex hydrogenation route and is a significant milestone for the improvement of this polymer modification technology. This study also provides a new route not only in chemical modification of SBR by using rhodium complex but in hydrogenation of other unsaturated polymers such as diene-based rubbers.

9.2 Recommendations for Further Research

Although some breakthrough and promising results have been achieved in this thesis, there are still many issues that are worthy of further investigation in order to establish a hydrogenation process that will be commercialized in the future. These are listed below:

a) About the formula of Rh hydrido complex that has been used in the present work, there is some doubt that what has been claimed is probably not what was synthesized. The main concern is the number of the ligands attached to the metal center, whether it is one, two or

three. So further analysis and characterization of the catalyst is highly recommended, using ^{1}H-NMR, ^{31}P-NMR and Rh-NMR;

b) Explore and understand the mechanism of cross-linking and gel formation reaction which is believed to be caused by the metal catalysts;

c) Search and screen more catalysts for hydrogenation of butadiene rubber, especially for the nitrile hydrogenation process. Based on the findings in the presents research, Rh is the best candidate catalyst, however, Ru complexes are still worthy of further exploration. Some preliminary work on this will be discussed later in this chapter;

d) Conduct a systematic kinetic and dynamic study for butadiene rubber hydrogenation so as to further optimize the experimental conditions and procedures;

e) Achieve batch hydrogenation of nitrile and vulcanization at the same time or continuously, which will be environmentally friendly and economical, and be a true revolution to the rubber industry. Some preliminary thoughts on vulcanization of HNBR will be discussed later in this chapter.

9.2.1 Catalyst Development

Nickel, palladium, platinum, iridium and many hydrides did not effectively hydrogenate both carbon-carbon double bonds and nitrile groups. Ruthenium and rhodium were the only complexes with high activity and minimal to zero gelling. Based on previous research and the results stated above rhodium complexes work best and will thus be the main consideration in finding a new catalyst. Furthermore, the complex should be either a standard 3 coordinate rhodium(I) catalyst or a 5 coordinate rhodium(III) catalyst with at least two hydrogen atoms. These restrictions were placed to help retain the hydrogenation ability of the catalyst and to retain similar structure to the current catalyst being used in this study.

The ligands on the metal center of a rhodium catalyst are the most important part in determining its reactivity. Phosphine groups are most commonly used as ligands as they are generally non-reactive in most environments and are easy to tailor to achieve specific properties.[151] Phosphine groups fall into two groups of ligands, σ-donors or π-acceptors. Using a strong π-acceptor will form large electronic densities spread out over the whole complex. Having a strong σ-donor will focus the electron density near the center metal of the complex. This increases reactivity toward addition of H_2, a necessary step in hydrogenation reactions.

The concept of the “Tolman Cone Angle” is widely accepted and is an important part in selecting a phosphine ligand[152] for catalysis. The angle is used as a measurement of steric size of the phosphine ligand. Essentially it is a way to describe the ligands “bulkiness”. A small angle correlates to a low level of bulkiness whereas a large angle is representative of a bulky ligand. Using a ligand with a different stereochemistry will of course affect the nature of the reactions and the products formed. In this way catalysts can be designed to perform certain tasks based on their ligand structure. Tolman also produced a famous chart depicting these cone angles based on the ligand used (note: ϕ indicates a phenyl group, Ph):

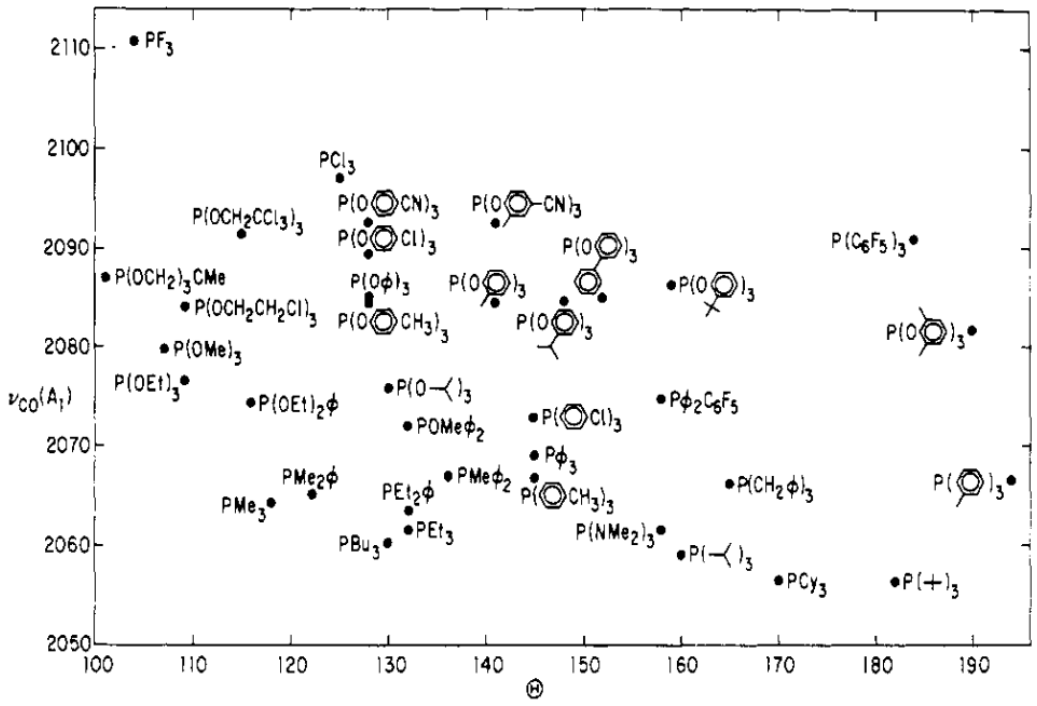


Figure 9-1 Tolman Cone Angle[152]

9.2.1.1 Dihydrochlorobis(tri-t-butylphosphine)rhodium(III) - $RhH_2Cl(PBu^t_3)_2$

This catalyst was chosen for a few reasons. First, it has reactivity toward hydrogenation of olefins, a necessary step in the reduction of NBR. Second, it has a very similar structure to the current catalyst being used. Instead of *i*-Pr groups it instead has *t*-Bu groups. This increases the steric interactivity to a higher Tolman cone angle. According to the graph, the catalyst being used has a cone angle of about 160 degrees, whereas $RhH_2Cl(PBu^t_3)_2$ has a cone angle of approximately 182 degrees.[153] This ligand is also a stronger σ-donor. Wilkinson’s catalyst has a reported ligand cone angle of about 145 degrees

and is selective toward olefins, failing to reduce the C≡N groups. Having a stronger σ-donor rather than a weaker one may solve this problem, though it is uncertain.

Masters *et al.* stated many of their five-membered rhodium(III) catalysts formed a square pyramidal structure, which seems consistent with the catalyst being used having a very similar square planar structure.[154] Formation of $RhH_2Cl(PtBu^t_2Me)_2$ produced a configuration very similar to $RhH_2X(PPh_3)_2$ (X = Cl, Br, I), an intermediate in the homogeneous catalyst $RhCl(PPh_3)_3$, however $RhH_2Cl(PBu^t_2Me)_2$ is shown to contain *cis*-triphenylphosphine ligands. Catalysts of this type are noted to be very active hydrogenation catalysts for olefins and do not need added base for activity. The synthesis and reactivity of this compound was also described by Masters *et al.*[154]

In summary, $RhH_2Cl(PBu^t_3)_2$ may be a good catalyst for the reduction of olefins and nitriles in NBR. It has a very similar chemical structure to the current catalyst $RhH(P(i\text{-}Pr)_3)_3$ indicating it may have a similar reactivity. $RhH_2Cl(PBu^t_3)_2$ has bulkier ligand groups that are stronger σ-donors which may increase reactivity and may help in ensuring primary amines are formed. $RhH_2Cl(PBu^t_3)_2$ is also fairly simple to synthesize according to the work of Masters *et al.*[154]

9.2.1.2 Chlorotris(tribenzylphosphine)rhodium(I) - $RhCl(PBz_3)_3$

Using PBz_3 ligand in rhodium-based catalysis is a relatively new and unexplored area of research. The use of the PBz_3 ligand in rhodium has been mostly overshadowed by its use in other metal complexes.[155] The structure of the PBz_3 group is very similar to that of PPh_3, except the cone angle is increased from about 145 degrees (PPh_3) to about 165 degrees (PBz_3). Muller *et al.* stated a cone angle in the 165-173 degree region supporting the measurement on the Tolman graph.[156] This angle makes the compound a stronger σ-donor than PPh_3 yet it remains close to the PPr^i_3 ligands 160 degrees. This suggests it will form a rhodium complex with similar properties that may be able to hydrogenate both the olefins and nitriles of NBR.

Zhou *et al.* reported the addition of hydrogen to the rhodium complex using H_2 gas to form $RhCl(H_2)(PBz_3)_3$, a rhodium(III) hydride complex.[157] This complex resembles very much the proposed mechanism for the catalyst used in this work and is a necessary step in hydrogenation. Landaeta *et al.*[155] used a similar, but bulkier ligand to test hydrogenation of cinnamaldehyde and compared it to the less bulky PBz_3. They reported that the PBz_3 ligand was very good for hydrogenating the olefins in cinnamaldehyde. This data further supports the notion that this complex will react as the same as the catalyst being used to reduce the olefins and nitriles in NBR. It has

almost the same bulkiness in ligand structure, forms similar intermediates and has a medium-strong σ-donating ability.

9.2.2 Vulcanization of Nitrile-Reduced HNBR

As stated in Chapter 2, an optimal amount ACN content in butediene rubber will be significant and beneficial to the vulcanization process, because it could make peroxide vulcanization, which is more environment-friendly than traditional sulfur process, much easier. As already stated in Chapter 2, vulcanization is a method to change the properties of rubber, usually NR or SBR, to make it stronger, more chemically resistant and more temperature resistant. These properties are achieved by creating cross-linking across the polymer chains. This cross-linking is most commonly formed in industry using sulfur bonds. It was found that heating rubber with sulfur caused drastic, positive changes in its inherent properties and has since been thoroughly studied. Some research has also been done to perform vulcanization using peroxides and other chemicals instead, though sulfur remains the most widely used additive.

There are many disadvantages to using sulfur for vulcanization. While many of these can be changed or fixed using various additives and curating techniques, some are unavoidable. There can also be complications from the type of rubber being used and its reactions with the additives being consumed during vulcanization. Vulcanization agents and other curatives must reach the rubber particles in the water phase, although they are relatively insoluble in both water and rubber.[158] This can cause slow vulcanization times and require agitation and sometimes heat to accomplish.[158] Furthermore these methods can be more expensive than other modifications of rubber and if the process is not done properly the rubber will become brittle instead of elastic.

Another major concern in vulcanization of rubber using sulfur is the safety of such a process. Carbon disulfide regarding thiono-sulfur-containing compounds like those used in cold vulcanization of rubber is especially dangerous. Neal *et al.*[79] stated, “Many toxic effects have been attributed to exposure to this compound. In addition to those already cited (enzyme inhibition and liver damage), CS_2 has been reported to cause neurological effects, visual defects, gastrointestinal symptoms, nephrosclerosis, clinical hypercorticism, anemia, an increase in coronary heart disease in man, and testicular atrophy in rats” .

Hydrogen sulfide is a gas often formed during the heating of rubber with sulfur. Fisher stated[80], “that hydrogen sulfide is present during vulcanization is shown by the odor of the gas during the heating of

a rubber-sulfur mix, especially when the press is opened, and also by the fact that certain metallic oxides such as zinc oxide, ferric oxide, and litharge are converted into the corresponding sulfides. These oxides are not converted into the sulfides by elemental sulfur at the temperatures used".[80] This gas is highly toxic as noted by the World Health Organization. In humans it is known to cause ocular effects, respiratory effects, neurological effects, cardiovascular effects, metabolic effects, reproductive effects and even cancer. Most of these are prominent from a one-time exposure to a high concentration of H_2S.[81]

The development of a hydrogenation process that both hydrogenates and vulcanizes the rubber at the same time has received some attention in the present study. While further vulcanization may be necessary, much less, if any, sulfuric compounds are needed to complete vulcanization. This method is cheaper, easier and much less harmful than using sulfur-based compounds. If some peroxides can be used as vulcanizing agent, it would be of great benefits and importance for environmental purpose.

Appendix A
Nomenclature

ACN	Acrylonitrile
a.k.a.	Also known as
ASTM	American standard test method
FT-IR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
HD	Hydrogenation degree
HNBR	Hydrogenated nitrile butadiene rubber
HSBR	Hydrogenated styrene butadiene rubber
MCB	Monochlorobenzene
MEK	Methyl ethyl ketone, butanone
Mn, Mw	Number average molecular weight, weight average molecular weight
NBR	Nitrile butadiene rubber
NMR	Nuclear magnetic resonance
NR	Natural rubber
Os	Osmium
$P(i\text{-}Pr)_3$, P^iPr_3, PPr^i_3, PP^ir_3	Triisopropylphosphine
PPh_3	Triphenylphosphine
psi	lb/in^2, pounds per square inch
psig	psi gauge
Rh	Rhodium
rpm	Rotation per minute
Ru	Ruthenium
SBR	Styrene butadiene rubber
THF	Tetrahydrofuran
TPP	Triphenylphosphine

Appendix B
Original Experimental Data

This research project is a confidential project sponsored by NSERC and Lanxess Inc. The original data for all experiments will only be provided in the copies that are used internally.

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